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The Electrochemical Fluorination of Benzenes and Pyridines[1]

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The electrochemical fluorination of several aromatic compounds (benzene, fluorobenzene, chlorobenzene, *m*-dichlorobenzene, anisole, *o*-chloroanisole, thiophenol, *p*-chlorothiophenol, *m*-thiocresol, 2-chloropyridine, and 3-chloropyridine) has been carried out. Perfluorocyclohexane was the principal product from benzene and fluorobenzene. In addition, chloro-derivatives of perfluorocyclohexane were produced from chlorobenzenes. Anisoles gave fully-saturated perfluoroethers, together with cleaved products. Extensive cleavage was observed in the fluorination of thiophenols and chloropyridines, and fluorocarbons and sulfur hexafluoride or nitrogen trifluoride were characteristic products. New compounds were also formed, trifluoromethyl 2-chlorodecafluorocyclohexyl ether from *o*-chloroanisole, and 3-chlorodecafluoropiperidine and 2-chloroundecafluoropentane from 3-chloropyridine.

Although a number of papers dealing with the fluorination of aromatic compounds with elemental fluorine[2] and with higher valency metallic fluoride[3] have appeared, works on the electrochemical fluorination of these compounds are rare. A patent[4] mentioned the electrochemical fluorination of several aromatic compounds, but no details were given. Shepard

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[1] Presented in part at the Autumn Meeting of the Chemical Society of Japan, Nagoya, October, 1971.

[2] a) L. A. Bigelow, "Fluorine Chemistry," Vol. 1, ed. by J. H. Simons, Academic Press, New York, N. Y., (1950), p. 380. b) J. M. Tedder, "Advances in Fluorine Chemistry," Vol. II, ed. by M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths Scientific Publications, London (1961), p. 129.

[3] a) M. Stacey and J. C. Tatlow, "Advances in Fluorine Chemistry," Vol. I, ed. by M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths Scientific Publications, London (1960), p. 166. b) W. A. Sheppard and C. M. Sharts, "Fluorine Organic Chemistry," W. A. Benjamin, New York, N. Y., (1969), p. 72.

[4] J. H. Simons, U. S. 2519983 (1950).

and Dannels,[5] and Kokhanov and Per'kova[6] have discussed a fluorine-containing polymer formed by the electrochemical fluorination of benzene. The difficulty of the fluorination of benzene itself by the electrochemical process has been described.[7] Soviet chemists have reported on the electrochemical fluorination of fluorinated anisole[8] and *N,N*-dimethylaniline,[9] but they have also described their failure in the fluorination of unfluorinated anisole.[8]

The present paper will deal with the electrochemical fluorination of benzene and its derivatives in order to clarify their behavior in the fluorination. For the sake of comparison with the fluorination of chlorobenzenes, the fluorination of chloropyridines was also included in the present work. Pyridine has often been subjected to electrochemical fluorination,[10] but no works on chlorinated pyridines have been reported.

The reaction conditions for the electrochemical fluorination of benzene and its derivatives, and pyridines, and the results obtained, are shown in Tables 1 and 2 respectively. Benzene was only slightly soluble in anhydrous hydrogen fluoride,[11] and the resulting solution did not have enough electric conductivity; therefore, its electrochemical fluorination required the use of a conductivity additive, sodium fluoride.

From benzene, perfluorocyclohexane, which consitituted a high percentage of the product composition, and perfluoro(methylcyclopentane) were produced, together with fragmented products. A considerable amount of tarry material in the cell and on the electrodes was also found. No simple fluorinated aromatic compound could be isolated. The formation of perfluorocyclohexane and perfluoro(methylcyclopentane) has also been reported in the electrochemical fluorination of 1,1-difluorocyclohexane.[7]

The mechanism for the fluorination of benzene to form perfluorocyclohexane may be of the free-radical type. The initial attack of the fluorine radical is presumably by direct addition to benzene nucleus to form the fluorocyclohexadienyl radical. This combines with the fluorine radical; the resulting intermediate is fluorinated further to yield hexafluorocyclohexane or a similar compound. The replacement of the hydrogens of the cyclohexane by fluorines follows to produce perfluorocyclohexane. The cleavage of the carbon-carbon bond probably occurs in this replacement stage by the energy which is liberated from the formation of the hydrogen-fluorine and carbon-fluorine bonds. Perfluoro(methylcyclopentane) may be yielded by the rearrangement of the carbon skeleton of partially-fluorinated cyclohexanes. The ease of the isomerization of the cyclohexane ring to methylcyclopentane has been established.[12]

No partially fluorinated products except trifluoromethane were obtained. Even if such compounds were formed, their amounts would be small and they would be dissolved in anhydrous hydrogen fluoride. The tarry material would be formed by radical mech-

Table 1. Conditions for fluorination

Run No.	Sample[a]	Voltage (V)	Electricity[b,c] passed (A. hr)	Procedure[d,e]
1	Benzene	5.2—9.0	64 (65)	A
2	Fluorobenzene	4.0—7.4	87	A
3	Chlorobenzene	4.8—6.1	94	A
4	*m*-Dichlorobenzene	4.9—5.8	106	A
5	Anisole	5.4—9.0	86 (74)	A
6	*o*-Chloroanisole	6.0—9.0	97 (85)	A
7	Thiophenol	5.0—6.3	131	B
8	*p*-Chlorothiophenol	6.2—6.8	131	B
9	*m*-Thiocresol	5.0—5.5	164	B
10	2-Chloropyridine	5.0—5.2	87	B
11	3-Chloropyridine	5.3—6.0	87	B

a) The amount of the starting material used was 0.20 mol except *o*-chloroanisole, 0.175 mol.

b) The amount of electricity supplied was 1.1 times of the theoretical one that was, as indicated below, assumed to be required to form perfluorocyclohexane from benzene and its derivatives, and undecafluoropiperidine from pyridines, respectively. For example,

$C_6ClH_5 + 18\,F \longrightarrow c\text{-}C_6F_{12} + 5\,HF + ClF$

$ClC_5H_4N + 16\,F \longrightarrow C_5F_{11}N + 4\,HF + ClF$

c) The anodic current density was adjusted as 1.2—1.5 A/dm^2; however, in runs 1, 5, and 6, the current block occurred. The numerical values in the parentheses shows the percentage of electricity used to the theoretical amount.

d) Cell temperature was kept at 5—8 °C.

e) A: sodium fluoride (10 g) was used; B: Carried out without using the additive.

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5) A. F. Shepard and B. F. Dannels, *J. Polym. Sci.*, A-1, **4**, 511 (1966); U. S. 3386899 (1968).

6) G. N. Kokhanov and S. A. Per'kova, *Electrokhimiya*, **3**, 977 (1967).

7) M. Sander and W. Blöchl, *Chem. Ingr. Tech.*, **37**, 7 (1965).

8) N. A. Ryabinin, I. P. Kolenko, L. N. Pushkina, V. F. Kollegov, and B. N. Lundin, *Zh. Obshch. Khim.*, **39**, 2716 (1969).

9) V. S. Plashkin, L. N. Pushkina, S. L. Mertsalov, V. F. Kollegov, and S. V. Sokolov, *Zh. Org. Khim.*, **6**, 1006 (1970).

10) See, for example, S. Nagase, "Fluorine Chemistry Reviews," Vol. 1, ed. by P. Tarrant, Marcel Dekker, New York, N. Y., (1967), p. 93.

11) Ref. 2-a), p. 239.

12) A. L. Glasebrook and W. G. Lovell, *J. Amer. Chem. Soc.*, **61**, 1717 (1939).

TABLE 2. RESULTS WITH THE FLUORINATION OF BENZENES AND PYRIDINES

Run No.	Product obtained (g)	Total[a] yield (%)	Product composition[b] (%)							
			Common product							Others
			CF_4	CHF_3	C_2F_6	C_3F_8	n-C_4F_{10}	n-C_5F_{12}	cyclo-C_6F_{12}	
1	7.1	15.4	11.1	18.0	1.6	1.0	1.3	+	54.2	n-C_6F_{14}(+), CF_3-cyclo-C_5F_9 (12.7)
2	17.7	29.2	5.3	0.7	0.3	0.9	+	+	74.1	n-C_6F_{14}(0.2), CF_3-cyclo-C_5F_9 (18.5)
3	15.6	27.4	3.4	2.0	0.5	0.2	0.2	1.8	40.6	n-C_6F_{14} (0.4), $CClF_3$ (5.6), CF_3-cyclo-C_5F_9 (3.5), cyclo-C_6ClF_{11} (41.8)
4	8.1	17.1	21.3	4.9	0.9	1.7	2.0	4.1	19.8	n-C_6F_{14} (2.1), $CClF_3$ (9.9), cyclo-C_6ClF_{11} (23.6), cyclo-$C_6Cl_2F_{10}$ (9.6)
5	9.1	15.1	30.1	0.2	+	+	+	0.3	0.8	n-C_6F_{14}(+), CF_3O-n-C_6F_{13} (7.9), CF_3O-cyclo-C_6F_{11} (60.4)
6	9.8	25.0	16.5	6.0	1.9	8.1	+	6.1	4.9	n-C_6F_{14} (1.7), $CClF_3$ (21.3), CF_3O-n-C_6F_{13} (6.2), CF_3O-cyclo-C_6F_{11} (12.4), cyclo-C_6ClF_{11} (5.6), CF_3O-cyclo-C_6ClF_{10} (9.3)
7	25.6	64.3	9.1	+	5.3	+	+	0.6	23.5	n-C_6F_{14} (+), CF_3-cyclo-C_5F_9 (2.3), SF_6 (59.2)
8	18.1	39.6	10.7					2.5	34.0	n-C_6F_{14} (+), CF_3-cyclo-C_5F_9 (1.5), cyclo-C_6ClF_{11} (13.1), $CClF_3$ (3.2), SF_6 (35.0)
9	34.4	94.6	30.3	+	+	+	+	+	2.0	CF_3-cyclo-C_6F_{11} (23.8), SF_6 (43.8)
10	16.6	52.7	3.0	+	+	+	1.5	26.6		$C_5F_{11}N$ (3.3), C_5ClF_{11} (7.7), $CClF_3$ (+), NF_3 (57.9)
11	16.0	49.0	6.2	9.3	+	+	1.4	15.8		$C_5F_{11}N$ (2.0), C_5ClF_{11} (19.8), $C_5ClF_{10}N$(+), NF_3 (45.4)

a) In the calculation, the total number of mole of the products including fragmented ones was divided by the mole of starting material fed.

b) Expressed in mole percent.

anism: the addition of the fluorine radical to the benzene nucleus occurs, and the fluorohexadienyl radical thus formed would attack benzene to produce another radical; this process could be repeated and would ultimately result in the formation of a highly polymerized material.

Halobenzenes and anisoles also produced considerable amounts of a resinous material. These aromatic compounds, similar to benzene, seemed to have only a limited solubility in anhydrous hydrogen fluoride. Their fluorinations were carried out by the use of the conductivity additive. Fluorobenzene was converted into perfluorocyclohexane in a better yield than benzene was. Chlorobenzene gave chloroundecafluorocyclohexane,[13] in addition to perfluorocyclohexane, together with cleaved products. 1,3-Dichlorodecafluorocyclohexane[13] was produced from *m*-dichlorobenzene in a small yield. The fluorination of *m*-dichlorobenzene was carried out with some difficulty. Explosions often occurred in the reaction system. Among the compounds subjected to the present fluorination, *m*-dichlorobenzene appeared to have the least solubility in anhydrous hydrogen fluoride. The generation of free fluorine was presumably the cause of the explosion.

The ether linkage was relatively stable in the electrochemical fluorination, and anisole and *o*-chloroanisole gave fully-fluorinated derivatives which retained the original ether linkage. *o*-Chloroanisole yielded a new compound, trifluoromethyl 2-chlorodecafluorocyclohexyl ether, but the yield was low. From these results, it may be stated that the chlorine in the aromatic nucleus is retained in the electrochemical fluorination, and chlorinated polyfluorocyclohexyl derivatives are given.

In contrast to the behavior of the compounds described above, thiophenol, *p*-chlorothiophenol, *m*-thiocresol, 2-chloropyridine, and 3-chloropyridine gave an electro-conducting solution as would be expected by their basic character. Therefore, their fluorinations were accomplished without using the conductivity additive. These thiophenols and pyridines afforded the perfluorinated products and did not yield any tarry material.

However, extensive cleavage occurred at the site of the hetero-atoms, such as nitrogen or sulfur, resulting in the formation of nitrogen trifluoride or sulfur hexafluoride, along with fluorocarbons. These phenomena may be caused mainly by the weakness of the carbon-nitrogen and carbon-sulfur bonds, whose single-bond energies are 69.7 and 62.0 kcal/mol respectively (carbon-carbon bond energy, 83.1 kcal/mol).[14] As has been shown in connection with the electrochemical fluorination of amines,[15] the adsorption of the hetero-compounds at the active sites on the nickel anode may give the conditions for the preferential attack of fluorine on the hetero-atoms.

As the principal products, thiophenol and *m*-thiocresol afforded perfluorocyclohexane and perfluoro(methyl-

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[13] a) J. C. Tatlow and R. E. Worthington, *J. Chem. Soc.*, **1952**, 1251. b) P. L. Coe, B. T. Croll, and C. R. Patrick, *Tetrahedron*, **20**, 2097 (1964).

[14] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, N. Y. (1960), p. 85.

[15] B. Chang, H. Yanase, K. Nakanishi, and N. Watanabe, *Electrochim. Acta*, **16**, 1179 (1971).

cyclohexane) respectively, in reasonable yields while *p*-chlorothiophenol yielded perfluorocyclohexane and chloroundecafluorocyclohexane. The formation of the perfluorocyclohexyl-[16] or chloropolyfluorocyclohexyl-derivative of sulfur hexafluoride could not be confirmed under the reaction conditions used. Chloropyridines yielded nitrogen trifluoride, perfluoropentane, and 1-chloro- or 2-chloroundecafluoropentane as the main products. 3-Chloropyridine gave a small amount of a new compound, 3-chlorodecafluoropiperidine.

Experimental

Materials and Apparatus. The starting materials subjected to the fluorination were all of a reagent grade. Their purities were confirmed by gas chromatography. Anhydrous hydrogen fluoride was more than 99.5% pure. The electrolytic cell used was the same as that described in a previous paper.[17] The product identifications and analyses were performed by means of gas chromatography (Shimadzu GC-2C model chromatograph) and IR spectroscopy (Hitachi EPI-S2 spectrometer), as before.[18] Mass spectrometry-(Hitachi RMU-7 spectrometer) was frequently used.

Procedure A (for a poor electro-conducting solution). As a typical example, the procedure for the fluorination of chlorobenzene (Run 3) will be described. In electrically-purified anhydrous hydrogen fluoride (1.28 l) in the cell, sodium fluoride (10 g) was dissolved. Then, while the current was being passed through the hydrogen fluoride solution, chlorobenzene (22.5 g, 0.20 mol) was charged in over a period of 2.5 hr by the use of a mechanical micro-pump.

The reflux condenser of the cell was kept at −15 °C. Helium (200 ml/min) was introduced through the bubbler placed at the bottom of the cell in order to agitate the solution and also to carry away the fluorinated products from the cell. In the begining of the electrolysis, the cell voltage was 4.8 V, with an anodic current density of 1.2 A/dm^2 (effective surface areas of the anodes and cathodes, 20 dm^2), and the cell temperature was 6—8 °C; however, the voltage rose gradually until it reached 6.1 V at the end of the operation. The total amount of electricity supplied over the 4-hr period was 94 A·hr. The passing of the cold brine through the reflux condenser was stopped for the last 30 min of the electrolysis. The blowing of helium was continued for 2 hr after the electrolysis was over.

The fluorinated products evolving from the cell were passed through the sodium fluoride tubes[17] (for the removal of the hydrogen fluoride) and gas-washing bottles (for the removal of a small amount of oxygen difluoride); these bottles were filled with an aqueous solution of sodium sulfite containing a small amount of potassium iodide. The products were further guided to a series of cold traps kept in ice and in liquid nitrogen.

The products thus obtained were separated into a lower-boiling (0.7 g) and a higher-boiling (14.9 g) fraction in the usual manner. The former was analyzed by gas chromatography, using a silica gel column at 80 and 120 °C, with helium as the carrier gas. It consisted of carbon tetrafluoride, trifluoromethane, chlorotrifluoromethane, perfluoroethane, perfluoropropane, and traces of other compounds. These and the compounds described below were identified by a comparison of their IR spectra (and of their mass spectra if necessary) with those of authentic specimens.

The higher-boiling portion was analyzed with a column packed with 30% of Daifl oil ♯50 (Daikin Industries Co.) on Chromosorb P-AW, 60—80 mesh (Johns-Manville Co.), at room temperature. It consisted of perfluorobutane, perfluoropentane, perfluoro(methylcyclopentane), perfluorohexane, perfluorocyclohexane, chloroundecafluorocyclohexane, and small amounts of unidentified compounds. The product distribution (mol%) and total yield are shown in Table 2, Run 3.

Most of the hydrogen fluoride used was distilled off from the cell, and the residual solution, containing much tarry material, was extracted with 1,1,2-trichloro-1,2,2-trifluoroethane and with ethyl ether; however, from the extract no pure individual compound was isolated.

By means of Procedure A, trifluoromethyl 2-chlorodecafluorocyclohexyl ether was obtained from *o*-chloroanisole (Run 6), although in a low yield (2.3%), together with cleaved products. The ether was a colorless liquid with a bp of 104 °C, n_D^{20} 1.3052. Found: Cl, 9.4; F, 64.0%; mol wt (mass), 382. Calcd for $C_7ClF_{13}O$: Cl, 9.3; F, 64.6%; mol wt, 382.5. The mass spectrum had peaks at 382 [M], 347 [M−Cl], 313 [M−CF_3], 247 [C_5F_9O], and 247 [C_5F_8Cl].

Procedure B (for an electro-conducting solution). As a representative example, the procedure for the fluorination of 3-chloropyridine (Run 11) will be described below. Several minor points were different from Procedure A. 3-Chloropyridine (22.7 g, 0.20 mol) was fed into the cell by the use of the micro-pump. The electrolysis was carried out with the anodic current density of 1.3 A/dm^2, the cell voltage of 5.3—6.0 V, and the cell temperature of 6 °C. Helium (200 ml/min) was blown into the cell.

The gases evolving from the cell were led to the sodium fluoride tubes, to gas-washing bottles filled with an aqueous solution of potassium hydroxide, to traps (Trap A) immersed in ice and in CO_2–acetone, to gas-washing bottles filled with an aqueous solution of sodium sulfite containing potassium iodide, and finally to traps (Trap B) immersed in ice and in liquid nitrogen. These were connected in a series. A total of 87 A·hr was consumed over a 3.5-hr period. Passing the cold brine through the reflux condenser was stopped for the last 30 min of the electrolysis, and the blowing of helium was continued for 1.5 hr after the electrolysis was over.

The product (11.0 g) obtained in Trap A was analyzed by means of a column packed with 30% of Daifl oil ♯50 on Chromosorb P–AW and one packed with 30% of dinonyl phthalate on Chromosorb P–AW at room temperature. It contained perfluoropentane, undecafluoropiperidine, and 2-chloroundecafluoropentane, together with small amounts of unidentified compounds. 3-Chlorodecafluoropiperidine was also detected, but its amount was very small and it was identified only by mass specrtometry. 2-Chloroundecafluoropentane, obtained in a 9.7% yield, was a colorless liquid with a bp of 61 °C, $n_D^{20}<1.28$. Found: Cl, 11.6; F, 68.1%; mol wt (mass), 304. Calcd for C_5ClF_{11}: Cl, 11.6; F, 68.6%; mol wt, 304.5. The mass spectrum had peaks at 304 [M], 285 [M−F], 269 [M−Cl], and 235 [M−CF_3].

The mass spectrum of 3-chlorodecafluoropiperidine had peaks at 299 [M], 280 [M−F], 264 [M−Cl], 261 [M−F_2], 245 [M−ClF], 183 [M−C_2F_3Cl], and 116 [C_2F_3Cl].

The product (5.0 g) in Trap B was analyzed by means of a silica gel column at 0 and 80 °C; it was found to consist of carbon tetrafluoride, trifluoromethane, perfluorobutane, and nitrogen trifluoride. The over-all results are shown in Table 2, Run 11.

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[16] R. D. Dresdner, T. M. Reed, III, T. E. Taylor, and J. A. Young, *J. Org. Chem.*, **25**, 1464 (1960).

[17] S. Nagase, H. Baba, K. Tanaka, and T. Abe, *Kogyo Kagaku Zasshi*, **67**, 2062 (1964).

[18] For example, S. Nagase, T. Abe, H. Baba, and K. Kodaira, This Bulletin, **43**, 2980 (1970).