# The Electrochemical Fluorination of Trifluoromethyl-substituted Benzenes

Michimasa YONEKURA,* Shunji NAGASE, Hajime BABA, Kazuo KODAIRA, and Takashi ABE
*Government Industrial Research Institute, Nagoya, Hirate-machi, Kita-ku, Nagoya 462*

(Received October 13, 1975)

The electrochemical fluorination of benzenes containing one or two trifluoromethyl groups has been carried out. They afforded perfluorocyclohexane derivatives with the trifluoromethyl group in good yields. Chlorobenzenes containing a trifluoromethyl group yielded chlorine-containing perfluorocyclohexane derivatives carrying the trifluoromethyl group. Trifluoromethylbenzonitriles gave perfluoro(dimethylcyclohexane)s, whereupon the nitrile group was converted into a trifluoromethyl group, thus releasing nitrogen trifluoride. The electrochemical fluorination of a trifluoromethylnaphthalene gave perfluoro(methyldecahydronaphthalene) only in a small yield.

Alicyclic fluorocarbons for practical use have received much attention, for example, in the electrical field,[1] because of their unique chemical inertness and physical properties. The preparation of these compounds by the electrochemical fluorination of aromatic hydrocarbons had been known to be unsatisfactory because of the conversion of the starting materials into tar in an electrolytic cell and the formation of polymeric substances on the surface of electrodes which impede the further smooth passage of the current. Sander and Blöch[2] obtained perfluoro compounds in good yields by the electrochemical fluorination of partially fluorinated cyclic alkanes.

In continuing our work on the electrochemical fluorination of aromatic compounds,[3] we have now found that the alicyclic fluorocarbons can be obtained in a reasonable yield by the fluorination of benzenes containing a trifluoromethyl group. However, in the case of the fluorination of trifluoromethyl-substituted naphthalene, the amount of the perfluorinated product was limited.

This report will further deal with the results of the electrochemical fluorination of (trifluoromethyl)benzenes carrying a nitrile group, which was found to be converted into a trifluoromethyl group by releasing nitrogen as nitrogen trifluoride during the fluorination. Thus, trifluoromethylbenzonitriles gave perfluoro-(dimethylcyclohexane)s. These perfluorocyclohexane derivatives have often been prepared by the exhaustive fluorination of cyclic hydrocarbons with high-valency metallic fluorides.[4]

## Results and Discussion

The trifluoromethyl group attached to the benzene nucleus had a good effect in increasing the yields of polyfluorinated products in the electrochemical fluorination. For example, benzylidyne trifluoride afforded perfluoro(methylcyclohexane) (I) in a 47.6% yield, together with a small amount of perfluoro(1,2-dimethylcyclopentane) (II). The results are shown in Table 1. The fragmented fluorocarbons, such as carbon tetrafluoride and hexafluoroethane, were among the by-products. No unsaturated fluorocarbons were isolated. The electrochemical fluorination of benzylidyne trifluoride could be carried out even without using a conductivity additive, such as sodium fluoride (Run 2).

Benzenes containing two trifluoromethyl groups gave the expected products, perfluoro(dimethylcyclohexane)s (Runs 3 and 4). As has been shown in the electrochemical fluorination of chlorobenzenes,[3] the chlorine atom attached to the benzene ring was retained during the fluorination, giving chlorine-containing perfluorocyclohexane derivatives. Thus, trifluoromethyl-substituted chlorobenzenes yielded chlorotrifluoromethyldecafluorocyclohexanes (Runs 5, 6, and 7). However, I was obtained as the main product. This indicates that the carbon–carbon bond between the trifluoromethyl group and the benzene ring of the chlorotrifluoromethylbenzenes is much more stable to the electrochemical fluorination than the carbon–chlorine bond.

The fluorination of these aromatic compounds may proceed by the successive addition of fluorine radicals to the benzene nucleus to produce partially fluorinated cyclohexane derivatives; the replacement of the hydrogens by fluorines is expected to follow, yielding perfluoro compounds. The cleavage of the carbon–carbon bond may occur in this replacement stage by means of the energy liberated by the formation of the hydrogen-fluorine and carbon-fluorine bonds. II is probably produced by the rearrangement of the carbon skeleton of the partially fluorinated cyclohexanes. Rearrangements like this have often been observed in the electrochemical fluorination of such cyclic compounds, for example, perfluoro(methylcyclopentane) from benzene.[3] The isomerization of the cyclohexane ring to methylcyclopentane has also been known.[5]

The fact that the benzenes stabilized by the trifluoromethyl group give perfluorocyclohexane derivatives in good yields in the electrochemical fluorination may be explained as follows. First, these compounds do not generate such radicals as fluorocyclohexylmethyl or benzyl, which, among others, seem to be responsible for tar formation. For example, toluene, which has been known to yield only a very small amount of $C_7$ fluorocarbons, but a considerable amount of tarry materials, in the electrochemical fluorination,[2,6] can be expected to produce radicals of this type. Second, the introduction of trifluoromethyl group to the benzene nucleus could give higher solubilities in anhydrous hydrogen fluoride than those of the corresponding aromatic hydrocarbons[7] because of the increased polarity of the molecule.

The trifluoromethyl group attached to the naphtha-

* Present address: Asahi Denka Kogyo Co., Ltd., 7-1, Higashiogu, Arakawa-ku, Tokyo 116.

TABLE 1. FLUORINATION OF TRIFLUOROMETHYL-SUBSTITUTED BENZENES

| Run No. | Starting material (mol) | Electricity passed (A·h) | Total amount of fluorocarbons obtained[b] (g) | Principal product | |
|---|---|---|---|---|---|
| | | | | Yield[c,d] (%) | Amount[f] (g) |
| 1 | Benzylidyne trifluoride(0.197) | 129 | 43.1 | I[e] 47.6, II 6.1 | 37.2 |
| 2 | Benzylidyne trifluoride(0.197) | 123[a] | 35.1 | I 34.8, II 11.9 | 32.2 |
| 3 | 1,3-Bis(trifluoromethyl)-benzene(0.197) | 148 | 25.2 | I 1.7, III 23.9 | 20.0 |
| 4 | 1,4-Bis(trifluoromethyl)-benzene(0.200) | 143 | 24.6 | I 1.8, perfluoro(1,4-dimethylcyclohexane)[e] 23.5 | 20.1 |
| 5 | 1-Chloro-2-trifluoromethyl-benzene(0.202) | 151 | 36.9 | I 27.7, II 2.2, 1-chloro-2-trifluoromethyl-decafluorocyclohexane 14.5 | 31.8 |
| 6 | 1-Chloro-3-trifluoromethyl-benzene(0.204) | 151 | 29.3 | I 19.1, II 1.1, 1-chloro-3-trifluoromethyl-decafluorocyclohexane 10.1 | 22.0 |
| 7 | 1-Chloro-4-trifluoromethyl-benzene(0.203) | 159 | 22.6 | I 16.8, II 1.0, 1-chloro-4-trifluoromethyl-decafluorocyclohexane 9.4, perfluorocyclohexane 0.6 | 20.0 |
| 8 | 1-Trifluoromethylnaphthalene (0.102) | 127 | 4.2 | perfluoro(1-methyldeca-hydronaphthalene) 4.4 | 2.3 |
| 9 | 2-Trifluoromethylbenzonitrile (0.204) | 150 | 10.8 | I 1.1, perfluoro(1,2-dimethylcyclohexane)[e] 9.7 | 8.7 |
| 10 | 3-Trifluoromethylbenzonitrile (0.188) | 150 | 27.8 | I 5.3, III 20.5 | 18.9 |
| 11 | 3,5-Bis(trifloromethyl)benzonitrile (0.199) | 150[a] | 4.2 | III 1.3, perfluoro(1,3,5-trimethylcyclohexane)[e] 2.6 | 3.4 |

a) Carried out without using the conductivity additive. b) Includes fragmented products such as $CF_4$ and $C_2F_6$. c) Yields were calculated as follows; (moles of respective product/moles of starting material) × 100. d) I=perfluoro(methylcyclohexane), II=perfluoro(1,2-dimethylcyclopentane), III=perfluoro(1,3-dimethylcyclohexane). e) IR spectra of these compounds agree with those listed in Ref. 13. f) Total amount of the principal products.

lene ring was not obviously effective. The electrochemical fluorination of 1-trifluoromethylnaphthalene afforded perfluoro(1-methyldecahydronaphthalene) only in a poor yield, 4.4% (Run 8). A considerable amount of tarry materials was found in the cell.

Trifluoromethylbenzonitriles are soluble in anhydrous hydrogen fluoride. In the fluorination, the carbon–nitrogen bond of the nitrile group was extensively cleaved, but the carbon–carbon bond between the benzene ring and the nitrile group remained intact; consequently, the nitrile group was converted into the trifluoromethyl group. The adsorption of the hetero-atom compounds at the active sites on the nickel anode may produce the proper conditions for the preferential attack of fluorine on the nitrogen atom.[8] Thus, perfluoro(dimethylcyclohexane)s (Runs 9 and 10) and perfluoro(1,3,5-trimethylcyclohexane) (Run 11) were obtained, but the yields of the products were depressed by the formation of a polymeric material. The presence of the nitrile group of the starting materials may assist the polymerization reaction.

## Experimental

*Materials and Apparatus.* 1-Trifluoromethylnaphthalene,[9] 3-trifluoromethylbenzonitrile, and 4-trifluoromethylbenzonitrile[10] were prepared according to the methods described in the literature. The other reagents were commercial products and were used as received. The anhydrous hydrogen fluoride was more than 99.5% pure.

The electrolytic cell used was similar to that described previously.[11] Analytical gas chromatography was carried out with a Shimadzu GC-2C chromatograph using Col. A [1.5 m (3 mm diam.), silica gel (60—80 mesh), 80—100 °C], and Col. B [6 m (3 mm diam), 15% Silicone DC QF-1 on Chromosorp P-AW (60—80 mesh), 25—50 °C]. For the semi-preparative work, a Shimadzu GC-1C chromatograph [10 m (6 mm diam), 25% Silicone DC QF-1 on Chromosorp P-AW (60—80 mech)], was used. The IR spectra were recorded on a Hitachi EPI-S2 spectrometer, and the mass spectra, on a Hitachi RMU-7 instrument at 70 eV, as before.[3]

*Fluorination of Trifluoromethyl-substituted Benzenes (Run 1).* To electrically purified anhydrous hydrogen fluoride (1.28 l) in the cell, sodium fluoride (10 g) was added, and, then benzylidyne trifluoride (28.8 g, 0.197 mol) was introduced into the cell continuously over a period of 2 h by means of a micro-pump in the early period of the reaction. This process was accompanied by the continuous passage of an electric current with an anodic current density of 0.9—1.4 A/dm$^2$ (the effective surface areas of the anodes and cathodes were each 20 dm$^2$), a cell voltage of 5.5—5.8 V, and a cell temperature of 5—7 °C. During the reaction, helium (150 ml/min) was blown into the cell through a bubbler, made of poly(tetrafluoroethylene) fiber, fitted in the bottom of the cell.

The gases evolving from the cell were passed through a reflux condenser kept at −15 °C and then consecutively through an iron tube packed with sodium fluoride pellets, polyethylene- and glass-made gas washing bottles filled with an aqueous solution of potassium sulfite containing a small amount of potassium iodide, and finally a series of cold traps immersed in ice and in liquid nitrogen respectively.

The products formed were sufficiently volatile under these conditions so that the major portion of them moved with the stream of hydrogen and the carrier gas of helium from the cell into these traps. The total quantity of electricity passed through was 129 A·h over a period of 5 h. After the electrolysis was over, the blowing of helium was continued for 1.5 h to forward the portion of the products still remaining in the reaction system.

The products (43.1 g) collected in the cold traps were separated into two fractions by trap-to-trap distillation. Each fraction was further subjected to gas-chromatographic analysis (the compositions were calculated on the basis of the chromatographic peak areas, assuming, as usual, equal weight sensitivities for all components),[12] using Col. A for the lower-boiling portion (1.4 g) and Col. B for the higher-boiling portion (41.6 g). The following compounds were thus obtained: $CF_4$ (0.6 g), $C_2F_6$ (0.1 g), $CHF_3$ (0.1 g), $CH_2F_2$ (0.1 g), *n*-$C_4F_{10}$ (trace), *n*-$C_5F_{12}$ (trace), $CF_3\overline{CF(CF_2)_3CFCF_3}$ (4.2 g), $\overline{CF_2(CF_2)_4CFCF_3}$ (33.0 g), and others (4.9 g, an unidentified complex mixture). These compounds were identified on the basis of their known IR spectra[13] or by a spectral comparison with authentic samples, as before.[3] The authentic sample of perfluoro(1,2-dimethylcyclopentane) was prepared by the electrochemical fluorination of *cis*-1,2-dimethylcyclopentane. Bp 72 °C (lit,[14] bp 71.5—71.8 °C). (All the boiling points are uncorrected). MS: *m/e* 331 [M−F], 281 [M−$CF_3$], 243 [$C_6F_9$), 231 [$C_5F_9$], and 219 [$C_4F_9$].

The procedures for the other runs (Runs 2, 3, and 4) were essentially the same as those described above; the results obtained for the principal products are shown in Table 1. (Run 2 was carried out without using sodium fluoride).

*Fluorination of Trifluoromethyl-substituted Chlorobenzenes (Run 5).* 1-Chloro-2-trifluoromethylbenzene (36.5 g, 0.202 mol) was fluorinated, in the presence of sodium fluoride (10 g), with an anodic current density of 1.1—1.5 A/dm², a cell voltage of 5.1—6.0 V, and a cell temperature of 7—8 °C. A total quantity of electricity of 151 A. hr was supplied for a period of 6 hr. The flow rate of helium was 150 ml/min. After the electrolysis was over, the blowing of helium was continued for 1.5 hr.

The products (33.8 g) in the cold traps were separated into lower- (1.7 g) and higher-boiling portions (32.2 g) by trap-to-trap distillation, and each was subjected to gas-chromatographic (Col. A, and Col. B) and spectral analyses. In addition to these products, a small amount of a clear, heavy liquid was drained from the cell through the drain-cock by breaking the bubbler; this liquid was washed with water and with an alkaline solution, dried over anhydrous sodium sulfate, and subjected to gas chromatography (Col. B). This portion (3.1 g) was found to consist of mostly 1-chloro-2-trifluoromethyldecafluorocyclohexane,[15,16] which was also obtained in the cold traps. Bp 103 °C (lit,[15] bp 103 °C). MS: *m/e* 366 [M], 347 [M−F], 331 [M−Cl], 312 [$C_7F_{12}$], and 297 [$C_6ClF_{10}$]. The summarized results of the analyses for these three portions of the products are as follows: $CF_4$ (0.5 g), $C_2F_6$ (0.6 g), $CClF_3$ (0.5 g), $CF_3\overline{CF(CF_2)_3CFCF_3}$ (1.6 g), $\overline{CF_2(CF_2)_4CFCF_3}$ (19.6 g), $\overline{CFCl(CF_2)_4CFCF_3}$ (10.7 g) and others (3.5 g). For the other runs (Runs 6 and 7), the results obtained for the principal products are shown in Table 1. The 1-chloro-3-trifluoromethyldecafluorocyclohexane obtained in Run 6 had a bp of 103 °C (lit,[16] bp 102—103 °C). MS: *m/e* 366 [M], 347 [M−F], 331 [M−Cl], 312 [$C_7F_{12}$], and 297 [$C_6ClF_{10}$]. The 1-chloro-4-trifluoromethyldecafluorocyclohexane obtained in Run 7 had a bp of 103 °C (lit,[16] bp 102—103 °C). MS: *m/e* 366 [M], 347 [M−F], 331 [M−Cl], 312 [$C_7F_{12}$], and 297 [$C_6ClF_{10}$].

*Fluorination of 1-Trifluoromethylnaphthalene.* By following procedures similar to those used for Run 1, 1-trifluoromethylnaphthalene (20.0 g, 0.102 mol) was fluorinated in the presence of sodium fluoride (10 g), with an anodic current density of 1.2—1.4 A/dm², a cell voltage of 5.0—6.8 V, and a cell temperature of 10—11 °C. A total quantity of electricity of 127 A·h was supplied for a period of 5 hr. The flow rate of helium was 50 ml/min.

After the electrolysis was over, most of the anhydrous hydrogen fluoride was distilled off from the cell; the remaining vaporizable residue was driven out with the helium carrier gas from the cell, which had been heated to 70 °C, into a polyethylene bottle containing water. A small amount of fluorocarbons was condensed at the bottom of the bottle. It was separated from water, washed with an alkaline solution, and dried over anhydrous sodium sulfate. This product (2.3 g) was found to consist of mostly perfluoro(1-methyldecahydronaphthalene) (Col. B, 100 °C), bp 159 °C (lit,[17] bp 161 °C). MS: *m/e* 512 [M], 493 [M−F], 443 [M−$CF_3$], 424 [$C_{10}F_{16}$], and 405 [$C_{10}F_{15}$]. The formation of possible isomers such as perfluoro(perhydroindan)s[2] could not be confirmed under the present conditions. From the tarry residue in the bottom of the cell, 1-trifluoromethylnaphthalene (9.5 g) was recovered unchanged by acetone extraction. No other isolable product was found. The products (1.9 g) obtained in the cold traps consisted of the following compounds: $CF_4$ (1.1 g), $C_2F_6$ (0.1 g), $CHF_3$ (0.2 g), $CH_2F_2$ (0.2 g), and others (0.3 g).

*Fluorination of Trifluoromethyl-substituted Benzonitriles (Run 9).* An initial portion of 3-trifluoromethylbenzonitrile was added into the cell, drop by drop, through a sampling valve; electrolysis was then carried out in the presence of sodium fluoride (10 g) with an anodic current density of 1.1—1.6 A/dm², a cell voltage of 5.3—7.2 V, and a cell temperature of 5—7 °C. After a 50 A·h electrolysis, a second portion of 3-trifluoromethylbenzonitrile was added to the cell to bring the total of the two portions to 32.2 g (0.188 mol), after which the electrolysis was continued. A total quantity of electricity of 150 A·h was supplied for a total period of 5.5 h. The flow rate of helium was 150 ml/min. After the electrolysis was over, the blowing of helium was continued for 1.5 h.

The products (27.8 g) obtained in the cold traps were separated into lower- (6.1 g) and higher-boiling portions (21.6 g) by trap-to-trap distillation, and each was subjected to gas chromatography (Col. A and Col. B). The following compounds were obtained: $CF_4$ (1.9 g), $NF_3$ (2.4 g), $C_2F_6$ (0.3 g), $CHF_3$ (0.8 g), $C_3F_8$ (0.5 g), *n*-$C_5F_{12}$ (trace), $\overline{CF_2(CF_2)_4CFCF_3}$ (3.5 g), $CF_3\overline{CFCF_2CF(CF_3)(CF_2)_2CF_2}$ (15.4 g), and others (2.9 g). Perfluoro(1,3-dimethylcyclohexane) had a bp of 101 °C (lit,[14] bp 101.7—101.9 °C). MS: *m/e* 381 [M−F], 331 [M−$CF_3$], 312 [$C_7F_{12}$], 293 [$C_7F_{11}$], and 281 [$C_6F_{11}$]. The results obtained for the principal products of this series of fluorinations (Runs 10 and 11) are shown in Table 1. (Run 11 was carried out without using sodium fluoride.)

The authors wish to thank the Daikin Industries Corporation for supplying the anhydrous hydrogen fluoride.

## References

1) a) S. W. Green, *Chem. Ind.*, No. 3, 63 (1969); b) M. Hill, *ibid.*, No. 3, 118 (1975).

2) a) M. Sander and W. Blöchl, *Chem. Ing. Tech.*, **37**, 7 (1965); b) Ger. Pat. 1119262 (1961).
3) Y. Inoue, S. Nagase, K. Kodaira, H. Baba, and T. Abe, *Bull. Chem. Soc. Jpn.*, **46**, 2204 (1973).
4) For example, M. Stacey and J. C. Tatlow, "Advances in Fluorine Chemistry," Vol. 1, ed. by M. Stacey, J. C. Tatlow, and A. G. Sharpe, Butterworths Scientific Publications, London (1960), p. 166.
5) A. L. Glasebrook and W. G. Lovell, *J. Am. Chem. Soc.*, **61**, 1717 (1939).
6) J. H. Simons, U. S. Pat. 2519983 (1950).
7) J. H. Simons, "Fluorine Chemistry," Vol. 1, ed. by J. H. Simons, Academic Press, New York (1950). p. 239.
8) B. Chang, H. Yanase, K. Nakanishi, and N. Watanabe, *Electrochim. Acta*, **16**, 1179 (1971).
9) K. Hosokawa and K. Inukai, 23th Annual Meeting of the Chemical Society of Japan, Tokyo, 1970, April, Abstracts, IV, p. 2264.
10) Y. Maki and K. Inukai, *Kogyo Kagaku Zasshi*, **67**, 807 (1964).
11) S. Nagase, H. Baba, K. Tanaka, and T. Abe, *Kogyo Kagaku Zasshi*, **67**, 2062 (1964).
12) K. Okazaki, S. Nagase, H. Baba, and K. Kodaira, *J. Fluorine Chem.*, **4**, 387 (1974).
13) IR spectra of perfluorocyclohexane derivatives [perfluoro- (methyl-, 1,2-dimethyl-, 1,4-dimethyl-, and 1,3,5-trimethyl-cyclohexanes)] are listed in "Infrared Spectral Data," American Petroleum Institute, Research Project 44, Carnegie Institute of Technology, 1959, Serial number 996—1003.
14) W. B. Burford III, R. D. Fowler, J. M. Hamilton, Jr., H. C. Anderson, C. E. Weber, and R. G. Sweet, *Ind. Eng. Chem.*, **39**, 319 (1947).
15) R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, **1956**, 61.
16) W. B. Ligett, U.S. Pat. 2654789 (1953).
17) E. T. McBee and L. D. Bechtol, *Ind. Eng. Chem.*, **39**, 380 (1947).