Electrochemical trifluoromethylation of aromatic compounds

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It was shown that the current yield of the products of anodic trifluoromethylation of arenes correlates with the adsorptivity and the rate of electrooxidation of arenes on the surface of a platinum electrode.

Key words: arenes, electrochemical trifluoromethylation.

Previously we have established that coelectrolysis of CF_3COOH and substituted benzenes containing one electron-withdrawing group in aqueous acetonitrile on a platinum electrode results in the products of trifluoromethylation, along with the normal products of trifluoroacetoxylation of the benzene ring,[1–3] especially in the case of aromatic compounds with strong electron-acceptor groups.[4]

It has been shown that acetonitrile, when adsorbing on a platinum anode in a wide range of potentials, inhibits the oxidation of molecules of water and aromatic compounds. As a result, the process of depolarization of an anode begins only at the oxidation potential of the trifluoroacetate anion and leads to generation of the trifluoromethyl radical. A competition between acetonitrile and aromatic compounds for a site on the electrode surface takes place. The electrolysis of triflouroacetic acid in the presence of aromatic compounds with one electron-withdrawing substituent resulted in the formation of isomeric products of trifluoromethylation, but it was impossible to introduce more than one trifluoromethyl group into the starting aromatic compound even during prolonged electrolysis.

In this work, an attempt was made to find correlations between the rates of oxidation, the adsorptivity on the electrode surface, and the yield of the products of trifluoromethylation of benzene derivatives containing one or two electron-withdrawing groups under the conditions of preparative electrolysis.

Results and Discussion

In order to compare the rates of electrooxidation of various arenes in aqueous-acetonitrile solutions of trifluoroacetic acid, the I,E dependences were recorded and the curves of partial polarization were plotted.

It follows from the data presented in Table 1 that the highest partial currents of oxidation are observed for acetophenone. As the electron-withdrawing ability of the substituent in the arene molecule increases, the rate of its oxidation decreases in the region of oxidation potentials of the trifluoroacetate anion, and in the case of benzotrifluoride, the total current of electrooxidation markedly decreases at the potential $E = 3.0$ V, indicating the inhibition of the oxidation of trifluoromethylacetate in the presence of benzotrifluoride. The kinetic data are in good agreement with the results of the preparative electrolysis. The current yields of the products of the trifluoromethylation of PhCN and $PhCF_3$ are equal to 62 and 35.5%, respectively[4] (the results for the other arenes are presented in the Experimental section).

The introduction of electron-withdrawing substituents into the benzene ring decreases the rate of adsorption. We determined the rate constants of adsorption (K_{ad}) and the limiting values of the coverage of the platinum electrode by some benzene derivatives containing one or two electron-withdrawing groups (Fig. 1):

Compound	K_{ad}/cm s^{-1} mol L^{-1}
PhCOMe	$2.4 \cdot 10^{-5}$
$PhCOCF_3$	$1.6 \cdot 10^{-5}$
$PhCF_3$	$5.6 \cdot 10^{-6}$
$1,3-(CF_3)_2C_6H_4$	$4.9 \cdot 10^{-6}$
$3-CF_3C_6H_4COMe$	$2.15 \cdot 10^{-6}$
$3-CF_3C_6H_4NO_2$	$2.47 \cdot 10^{-6}$

Conditions: aqueous solution 0.5 *M* CF_3COOH + 0.05 *M* CF_3COOK, $E_r = 0.4$ V.

The studies were carried out in aqueous solutions of CF_3COOH on a platinum electrode at the potentials preceding the oxidation of aromatic compounds in order to rule out the uncertainty caused by the possible adsorption of the oxidation products.

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Table 1. Partial currents of electrooxidation (*I*) of aromatic compounds and of the CF_3COO^- anion in the region of potentials (E_r/V) generating the trifluoromethyl radical (aqueous-acetonitrile solution 0.5 *M* CF_3COOH + 0.05 *M* CF_3COOK, the ratio MeCN : H_2O = 1 : 2, and the concentation of arenes, $7.4 \cdot 10^{-1}$ mol L^{-1})

Compound	I/mA cm^{-2}		
	E_r = 2.8	E_r = 2.9	E_r = 3.0
PhCOMe	21.02	20.7	21.3
$PhNO_2$	7.7	12.5	16.2
PhCN	7.3	12.4	14.8
$PhCF_3$	4.1	6.4	5.3
$PhCOCF_3$	13.05	14.01	8.9
CF_3COO^-	0.5	3.5	8.7

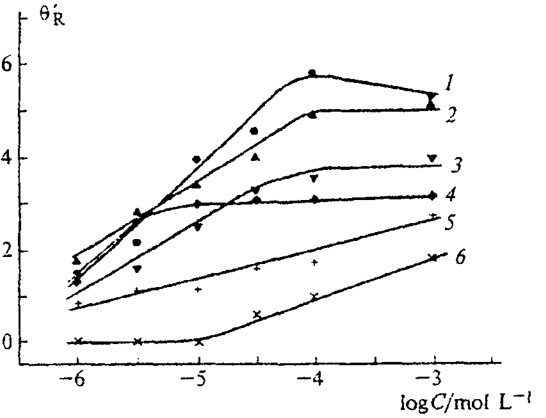


Fig. 1. Steady-state coverage of the surface of a plain platinum electrode by species of aromatic compounds as a function of their volume concentration in an aqueous solution 0.5 *M* CF_3COOH + 0.05 *M* CF_3COOK at 25 °C and potential E_r = 0.4 V: PhCN (*1*); PhCOMe (*2*); $PhCOCF_3$ (*3*); $PhNO_2$ (*4*); $PhCF_3$ (*5*); 1,3-$(CF_3)_2C_6H_4$ (*6*).

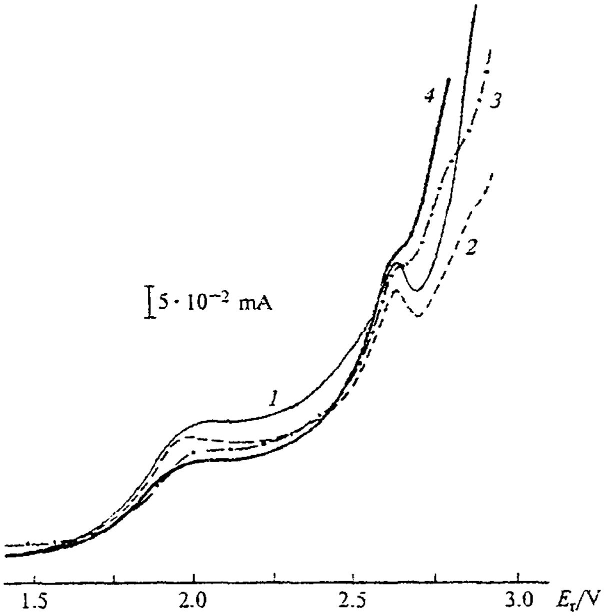


Fig. 2. Anodic polarization curves for a platinum electrode ($S = 3\times10^{-2}$ cm^2) in an aqueous-acetonotrile solution 0.5 *M* CF_3COOH + 0.05 *M* CF_3COOK (H_2O : MeCN = 11 : 4) in the absence (*1*) and in the presence of aromatic compounds: 1,3-$(CF_3)_2C_6H_4$, $4.3 \cdot 10^{-1}$ mol L^{-1} (*2*); 3-$CF_3C_6H_4NO_2$, $4.8 \cdot 10^{-1}$ mol L^{-1} (*3*); 3-$CF_3C_6H_4COOMe$, $4.9 \cdot 10^{-1}$ mol L^{-1} (*4*). The velocity of potential scanning is 100 mV s^{-1}.

Studies performed by the fast pulse electrochemical technique[5] showed that the adsorption of substituted arenes is well described by the Temkin isotherm

$$\theta_R = a + 1/f \ln c.$$

As can be seen in Fig. 1, the adsorptivity of arenes decreases as the electron-withdrawing ability of a substituent in the benzene ring increases. It is commonly accepted[6] that aromatic compounds are adsorbed on platinum in the region of high anodic potentials. However, this fact is generally due to the adsorption of the oxidation products rather than the true adsorption of the starting arenes. Therefore, we did not investigate the adsorptivity of aromatic compounds at the oxidation potentials (*E*/V) of carboxylate ions, especially as the coverage of the surface by adsorbed species in this region of potentials is very small and is comparable to the accuracy of the method used.

At the potential E_r = 0.4 V, the limiting coverage of the surface of a plain platinum electrode by the adsorbed species of aromatic compounds containing two electron-acceptor groups does not exceed 15% (see Fig. 1).

These data were obtained in an aqueous solution of potassium trifluoroacetate acidified by trifluoroacetic acid, however, they correlate well both with the results of the study of the kinetics of the electrooxidation of the same aromatic compounds in an aqueous-acetonitrile solution of potassium trifluoroacetate acidified by trifluoroacetic acid and with the results of preparative electrosynthesis in the region of potentials at which trifluoromethyl radicals are generated.

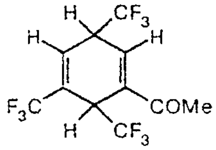
Figure 2 shows that noticeable currents of the electrooxidation of ArH in the region of the generation of trifluoromethyl radicals are observed only for 3-$CF_3C_6H_4COMe$, when it is present in significant concentrations in the electrolyte solution. The total currents of the oxidation of 1,3-$(CF_3)_2C_6H_4$ and 3-$CF_3C_6H_4NO_2$ in the region of potentials at which trifluoromethyl radicals are generated are even lower than that of the starting background curve. This may indicate that the aromatic compounds mentioned do not participate in the electrode process but only occupy a part of the surface due to adsorption, decreasing the oxidation rate of the trifluoroacetate anion.

The preparative electrolysis of aromatic compounds containing two electron-withdrawing groups showed that a decrease in their adsorptivity, in spite of the simultaneous decrease in the oxidation rate in the region of potentials at which trifluoromethyl radicals are generated, results in a decrease in the yield of the products of trifluoromethylation. This is likely due to both a decrease in the adsorptivity of these derivatives and spatial hindrances to attack by the trifluoromethyl radical. At the same time, as should be expected, the fraction of the products of trifluoromethylation of the benzene ring sharply decreases in the case of arenes containing two electron-withdrawing substituents. It seems that the mechanism of the radical electrochemical trifluoromethylation of arenes with two electron-withdrawing groups does not differ from that described by us previously.[4]

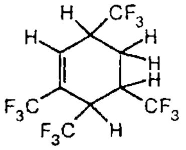
In spite of their comparatively low adsorptivity, these arenes accept electrochemically generated radicals to a greater extent than arenes containing one electron-withdrawing substituent. In other words, in this case, the aromatic compounds are not oxidized electorchemically but, when adsorbed on the surface of the electrode, take part in radical trifluoromethylation.

The formation of *ortho-*, *meta-*, and *para*-isomers whose ratio is close to that for common free-radical reactions (*cf.* Ref. 4) is evidence for the free-radical nature of the reactions of anodic trifluoromethylation.

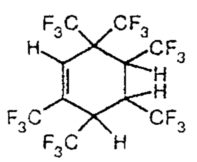
The introduction of a fourth substituent into the molecule of an aromatic compound under the conditions of anodic radical addition results in the formation of the cyclohexadiene derivatives (structures **A**, **B**, **C**, and **D**, see Experimental).



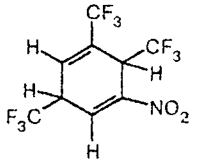
A



B



C



D

Similar results were previously obtained in studies of the reaction of thermally generated C_6F_{13} radicals with benzene[7] and the reaction of cathodically generated perfluoroalkyl radicals during reduction of high perfluoroalkylhalides in the presence of benzonitrile as a solvent.[8]

Preparative trifluoromethylation on a glassy-carbon anode GC-2000, which possesses low adsorption ability,[9] leads to a sharp decrease in the yield of the products of trifluoromethylation even in the case of aromatic compounds containing one electron-withdrawing group. This gives evidence for the important role of the adsorption of aromatic compounds in the anodic trifluoromethylation of arenes.

Thus, the yields of the products of anodic trifluoromethylation of arenes correlate with their adsorptivities and the rates of electrooxidation on the electrode surface: the higher the adsorptivity and the lower the rate of electrooxidation of the aromatic compound in the region of potentials at which trifluoromethyl radicals are generated, the higher the yield of the products of trifluoromethylation.

The anodic trifluoromethylation of benzene derivatives containing two electron-withdrawing substituents is not accompanied by oxidation of the aromatic compound (except for 3-trifluoromethylacetophenone) under the conditions of Kolbe electrosynthesis. The electrochemical inertness of arenes that do not participate in the electrode process when adsorbed onto the surface of an electrode allows them to play the role of acceptors of $CF_3\cdot$ radicals in this reaction.

Experimental

To measure voltammograms, we used a 25 mL glass three-electrode cell with a thermostating water jacket and separated anodic and cathodic spaces equipped by a sparger for purging inert gas. The glassy-carbon electrodes were embedded into Teflon, and the platinum electrodes were sealed with glass. Prior to measurements, the platinum electrodes were treated with a hot mixture of concentrated H_2SO_4 and H_2O_2 and were thoroughly washed with bidistilled water. Before recording voltammograms in aqueous and aqueous-organic media the platinum electrode was subjected to cathodic-anodic activation to obtain reproducible results, *viz.*, by alternative treatment for 5 s at 1.5 V and 0 V potentials, for a total duration of 60 s, they were then kept at 0.4 V for 200 s and at 0 V for 10 s; after that the curves were recorded. Before measurements in acetonitrile, the glassy-carbon electrode was treated with hot alkali, then washed with bidistilled water and thoroughly dried in a vacuum-dessicator. Before measurement of voltammograms, all the solutions were thoroughly purged with purified argon to remove oxygen. Potentials were measured relative to a hydrogen electrode in the same solution.

The adsorption of aromatic compounds in the double-layer region was studied by the potentiodynamic method[5] at the potential rate of 10 V s^{-1}. Before the potentiodynamic pulse was applied, the platinum electrode was subjected to cathodic-anodic activation according the above scheme; however, after the electrode was kept at 0.4 V, the potentiodynamic pulse was taken in a cathodic direction to 0 V. This program of treatment of the electrode prior to the application of the potentiodynamic pulse provided a clean surface before adsorption.

For the preparative electrosynthesis, 30—100 mL glass electrochemical cells equipped with a water jacket and a reflux condenser were used. During electrosynthesis with the use of a diaphragm, the cathodic and anodic spaces were separated with a Nafion-117 type membrane. The electrolyte was magnetically stirred. Platinum gauze electrodes and the electrodes made of plates of GC-2000 glassy carbon were used for preparative electrosynthesis. The sizes of the electrodes and the conditions of electrolysis are presented below. Before the electrosynthesis, the platinum electrodes were treated in the flame of a gas burner to remove the traces of impurities.

Voltammograms were recorded with a Pi-50.1 potentiostat on an N-308 two-coordinate recorder. The same potentiostat was used for electrosynthesis under galvanostatic conditions.

The adsorption measurements were carried out with a pulse potentiostat of the Institute of Electrochemistry, Russian Academy of Sciences.

The products of electrosynthesis were analyzed by GLC (gaseous products, Poropak Q, 30 °C; liquid products, 10% FS-1265 on Chromosorb or Kraytox). When the concentration of the products of trifluoromethylation in a solution after electrolysis was small, they were identified by GC-MS. The mass-spectra were registered on a V-6-7070 mass-spectrometer (70 eV, stationary phase OV-101, 30—5 °C min^{-1}). The ^{19}F NMR spectra were recorded on a Bruker WP-200 SY spectrometer (188 MHz), CF_3COOH as the external standard.

Acetonitrile for electrochemical measurements and preparative electrolysis was purified by treatment with $KMnO_4$ followed by double distillation over P_2O_5.

CF_3COOH and H_2O were twice distilled. All the aromatic compounds were purified according to the common procedures.

Anodic trifluoromethylation of acetophenone (AP) was carried out in a diaphragmic electolyzer with an ion-exchange Nafion-117 membrane. Anolyte composition: CF_3COOH, 5.7 g (0.05 mol); CF_3COOK, 1.18 g (0.0078 mol); PhCOMe, 5.17 g (0.042 mol); MeCN : H_2O = 9 : 1 (40 mL). The catholyte was an aqueous solution of 0.5 *M* CF_3COOH+0.05 *M* CF_3COOK. The anode was platinum gauze with a surface of 6 cm^2, the cathode was made of GC-2000 glassy carbon with a surface of 20 cm^2. The current density was 33 mA cm^{-2}; the temperature was 25 °C. During electrolysis, 0.072 F of electricity was passed through the solution, then the electrolyte was poured into an aqueous solution of $CaCl_2$ and three times extracted with ether; the extracts were three times washed with water and dried with $MgSO_4$. After evaporation, 1.75 g of a liquid was obtained. According to GLC, the products that differ from the starting substance are observed as traces are isomers of trifluoromethylacetophenone. ^{19}F NMR data, δ: −18.8 (s, *o*-CF_3); −14.3 (s, *m*-CF_3); −14.0 (s, *p*-CF_3), the ratio of the integral intensities was *o* : *m* : *p* = 9 : 6 : 7

In the mass-spectrum, the starting acetophenone was found along with products of trifluoromethylation with the formula $CF_3C_6H_5COMe$ (the separation of isomers was not successful). MS, m/z (I_{rel} (%)): 188 $[M]^+$ (18), 173 $[M-CH_3]^+$ (100), 145 $[M-COCH_3]^+$ (50), 126 $(C_6H_4CF_2]^+$ (8), 95 $[C_6H_4F]^+$ (10), 75 $[C_6H_3]^+$ (9), 43 $[COCH_3]^+$ (30).

No products containing two trifluoromethyl groups in the acetophenone molecule were found.

The anodic trifluoromethylation of acetophenone is accompanied by strong resinification, likely due to electrooxidation of the aromatic compound, which is in line with the partial currents for acetophenone taken from the voltammograms.

Anodic trifluoromethylation of nitrobenzene (NB). 6.25 g (0.05 mol) of nitrobenzene was added to the anolyte. The other conditions of electrolysis were the same as in the above example. A total of 0.082 F of electricity was passed through the solution. After treatment of the electrolyte as in the case of AP, 4.24 g of a liquid was separated, 10% of which was, according to GLC, a mixture of the isomers of trifluoromethylnitrobenzene. ^{19}F NMR, δ: −16.7 (s, *o*-CF_3); −13.7 (s, *m*-CF_3); −13.5 (s, *p*-CF_3); the ratio of integral intensities was *o* : *m* : *p* = 12 : 5 : 9. In the mass-spectrum, the starting nitrobenzene and two products corresponding by their masses to two isomers of trifluoromethylnitrobenzene with identical mass-spectra were observed: m/z (I_{rel} (%)): 191 $[M]^+$ (55), 172 $[M-F]^+$ (10), 161 $[M-NO]^+$ (10), 145 $[M-NO_2]^+$ (100), 95 $[C_6H_4F]^+$ (25), 75 $[C_6H_3]^+$ (19), 69 $[CF_3]^+$ (9), 30 $[NO]^+$ (22).

During electrolysis, 0.95 g (0.0083 mol) of CF_3COOH was consumed, the current yield based on the electrochemically generated trifluoromethyl radical was equal to 10.4%, the yield of trifluoromethylnitrobenzenes based on the CF_3COOH consumed was 23%, and the conversion of nitrobenzene was 22.8%.

No products containing two trifluoromethyl groups in the benzene ring were found.

Anodic trifluoromethylation of trifluoroacetophenone (TAP) was carried out in a diaphragmic electrolyzer, as was described for AP, and 8.8 g (0.05 mol) $PhCOCF_3$ was added to the anolyte. A total of 0.093 F of electricity was passed through the solution. During electrolysis, the electrolyte became dark brown, and 4.3 g of a liquid was obtained, 2% of which was, according to GLC, products of trifluoromethylation. ^{19}F NMR, δ: −17.5 (s, *o*-CF_3); −13.2 (s, *m*-CF_3); −12.7 (s, *p*-CF_3), the ratio of the integral intensities was *o* : *m* : *p* = 6 : 5 : 3. The mass-spectra of the separated products corresponded to the starting trifluoroacetophenone and to isomeric trifluoromethyltrifluoroacetophenones with identical mass-spectra: $CF_3C_6H_4COCF_3$ m/z (I_{rel} (%)): 223 $[M-F]^+$ (10), 173 $[M-CF_3]^+$ (100), 145 $[M-COCF_3]^+$ (95), 95 $[C_6H_4F]^+$ (15), 69 $[CF_3]^+$ (9).

During electrolysis, 0.013 mol of CF_3COOH was consumed. The current yield per electrochemically generated trifluoromethyl radical was equal to 14.7%, the yield of trifluoromethyltrifluoroacetophenones per CF_3COOH consumed was 4%, and the conversion of $PhCOCF_3$ was 51%.

Anodic trifluoromethylation of 3-trifluoromethylacetophenone (TMAP). Because of the easy electrochemical reduction of the keto group, the anodic trifluoromethylation of 3-trifluoromethylacetophenone was performed in a diaphragmic electrolyzer supplied with an ion-exchange Nafion-117 membrane. Anolyte composition: CF_3COOH, 5.7 g (0.05 mol); CF_3COOK, 1.18 g (0.0078 mol); 3-$CF_3C_6H_4COMe$, 7.5 g (0.039 mol); MeCN : H_2O = 9 : 1 (40 mL). The catholyte was an aqueous solution of 0.5 *M* CF_3COOH + 0.05 *M* CF_3COOK. The anode was platinum gauze with a surface of 6 cm^2, the cathode was made of GC-2000 glassy carbon with a surface of 20 cm^2. The current density was 50 mA cm^{-2} and the temperature was 25 °C. The total amount of electricity passed was 0.083 F. After the electrolysis was completed, the anolyte was treated in the same way as in the case of AP. After evaporation of ether, 6.7 g of an organic liquid was obtained 3% of which was, according to GLC, products of trifluoromethylation.

Using GC-MS, the starting 3-trifluoromethylacetophenone and the products of its trifluoromethylation, $(CF_3)_2C_6H_3COMe$ (two isomers), were determined, m/z (I_{rel} (%)): 256 $[M]^+$ (15), 241 $[M-CH_3]^+$ (100), 237 $[M-F]^+$ (19), 213 $[(CF_3)_2C_6H_3]^+$ (43), 163 $[CF_3C_6H_3F]^+$ (20), 144 $[CF_3C_6H_3]^+$ (8); 125 $[CF_2C_6H_3]^+$ (5); 43 $[COCH_3]^+$ (35); products (traces) with empirical formula: $\underline{(CF_3)_2C_6H_2(OH)COCH_3}$, m/z (I_{rel} (%)): 272 $[M]^+$ (15), 257 $[M-CH_3]^+$ (100), 253 $[M-F]^+$ (8), 229 $[(CF_3)_2C_6H_2(OH)]^+$ (5), 163 $[CF_3C_6H_3F]^+$ (40), 145 $[CF_3C_6H_4]^+$ (13), 43 $[COCH_3]^+$ (42); $\underline{(CF_3)_3C_6H_4COCH_3}$, m/z (I_{rel} (%)): 326 $[M]^+$ (10), 311 $[M-CH_3]^+$ (50), 307 $[M-F]^+$ (12); 263 $[M-CH_3CO-F-H]^+$ (5), 257 $[M-CF_3]^+$ (5), 241 $[M-2CF_3-H]^+$ (8), 237 $[M-CF_3-F-H]^+$ (25), 213 $[M-CH_3CO-CF_3-H]^+$ (12), 195 $[M-CH_3CO-CF_3-F]^+$ (8), 173 $[M-CH_3-2\ CF_3]^+$ (5), 145 $[M-CH_3CO-2CF_3]^+$ (15), 43 $[COCH_3]^+$ (100).

The introduction of the fourth substituent (the third trifluoromethyl group) results in the violation of aromaticity and likely the formation of the cyclohexadiene structure A (see above).

Anodic trifluoromethylation of 1,3-bis(trifluoromethyl)benzene (BTMB). The preparative electrolysis was carried out in a diaphragmless electrolyzer of 50 mL volume equipped with a reflux condenser and a magnetic stirrer. A platinum anode with a surface of 20 cm^2 and a nickel cathode (a wire with a surface of 2 cm^2) were used. The composition of the electrolyte: CF_3COOH, 5.7 g (0.05 mol); CF_3COOK, 1.18 g (0.0078 mol); 1,3-$(CF_3)_2C_6H_4$, 10 g (0.050 mol); MeCN : H_2O = 9 : 1 (40 mL).

The electrolysis was performed in the amperostatic regime: the current density was 12.5 mA cm^{-2} and the temperature was 25 °C. The electrolyte solution was magnetically stirred and after passing 0.084 F of electricity was treated as in the case of AP. After evaporation of ether, 9.5 g of a liquid was obtained 4% of which was, according to GLC, products of trifluoromethylation.

Using GC-MS, the starting 1,3-bis(trifluoromethyl)benzene and the products of its trifluoromethylation, $\underline{(CF_3)_3C_6H_3}$ (three isomers), were found, *m/z* (I_{rel} (%)): 282 $[M]^+$ (100), 263 $[M-F]^+$ (95), 244 $[M-2F]^+$ (3), 232 $[M-CF_2]^+$ (29), 213 $[M-CF_3]^+$ (100), 194 $[M-CF_3-F]^+$ (10), 163 $[M-CF_2-CF_3]^+$ (20), 144 $[M-2CF_3]^+$ (25), 125 $[M-2CF_3-F]^+$ (20), 99 $[C_8H_3]^+$ (5), 69 $[CF_3]^+$ (12); products (traces) with empirical formula $\underline{(CF_3)_4C_6H_6}$, *m/z* ($I_{rel}$ (%)): 333 $[M-F-2H]^+$ (15), 313 $[M-2F-3H]^+$ (5), 283 $[M-CF_3-2H]^+$ (25), 263 $[M-CF_3-F-2H]^+$ (20), 245 $[M-CF_3-2F-2H]^+$ (5), 213 $[M-2CF_3-3H]^+$ (7), 195 $[M-2CF_3-F-2H]^+$ (75), 163 $[M-2CF_3-CF_2-3H]^+$ (5), 145 $[M-3CF_3-2H]^+$ (15), 119 $[C_2F_5]^+$ (5), 75 $[C_6H_3]^+$ (8), 69 $[CF_3]^+$ (100), 51 $[CF_2H]^+$ (5), which corresponds to structure **B** (see above) and isomers with empirical formula $\underline{(CF_3)_6C_6H_4}$, *m/z* ($I_{rel}$ (%)): 471 $[M-F]^+$ (15), 451 $[M-2F-H]^+$ (12), 421 $[M-CF_3]^+$ (5), 402 $[M-CF_3-F]^+$ (18), 401 $[M-CF_3-F-H]^+$ (15), 383 $[M-CF_3-2F]^+$ (9), 333 $[M-2CF_3-F]^+$ (35), 313 $[M-2CF_3-2F-H]^+$ (9), 299 $[C_6\ (CF_3)_3F]^+$ (14), 279 $[C_6(CF_3)_3]^+$ (7), 263 $[(CF_3)_2C_6H_3CF_2]^+$ (17), 245 $[(CF_3)_2C_6H_4CF_3]^+$ (4), 213 $[(CF_3)_2C_6H_3]^+$ (5), 195 $[CF_2\ C_6H_4CF_3]^+$ (5), 163 $[C_6H_3CF_3F]^+$ (4), 132 $[C_6H_3F_3]^+$ (4), 69 $[CF_3]^+$ (100), which can correspond to structure **C** (see above).

Aromaticity is violated in structures **B** and **C** due to the introduction of two or more trifluoromethyl groups into the bis-trifluoromethylbenzene molecule.

Anodic trifluoromethylation of 3-trifruoromethylnitrobenzene (TMNB). The preparative electrolysis was carried out under the same conditions used for AP with the difference that 8.2 g (0.042 mol) of 3-$CF_3C_6H_4NO_2$ was introduced into the anolyte. The preparative electrolysis was performed at the current density 50 mA cm^{-2} and at 25 °C; 0.1 F of electricity was passed through the solution. After the electrolysis, the electrolyte was treated similarly to AP. After evaporation of ether, 7.8 g of a liquid was obtained 5% of which was, according to GLC, products of trifluoromethylation.

According to GC-MS, the starting trifluoromethylnitrobenzene was found along with the products of its trifluoromethylation, $\underline{(CF_3)_2C_6H_3NO_2}$, (two isomers), *m/z* ($I_{rel}$ (%)): 259 $[M]^+$ (15), 240 $[M-F]^+$ (5), 213 $[M-NO_2]^+$ (25), 163 $[M-CF_2-NO_2]^+$ (30), 144 $[M-CF_3-NO_2]^+$ (5), 69 $[CF_3]^+$ (10), 30 $[NO]^+$ (30); products with empirical formula $\underline{(CF_3)_3C_6H_4NO_2}$, *m/z* ($I_{rel}$ (%)): 327 $[M-2H]^+$ (10), 308 $[M-F-2H]^+$ (11), 281 $[M-NO_2-2H]^+$ (18), 258 $[M-CF_3-2H]^+$ (35), 240 $[M-CF_3-F-H]^+$ (20), 231 $[M-CF2-NO2-2H]^+$ (30), 213 $[M-CF3-NO2-H]^+$ (75), 194 $[M-CF_3-NO_2-F-H]^+$ (5), 181 $[M-2CF2-NO2-2H]^+$ (5), 163 $[M-CF3-CF2-NO2-H]^+$ (25), 143 $[M-2CF_3-NO2]^+$ (18), 99 $[CF_3]^+$ (5), 69 $[CF_3]^+$ (12), 46 $[NO_2]^+$ (15), 30 $[NO]^+$ (70), which could correspond to structure **D** (see above), and the product of the radical replacement of the nitro group, $\underline{(CF_3)_3C_6H_3}$, *m/z* ($I_{rel}$ (%)): 282 $[M]^+$ (70), 263 $[M-F]^+$ (70), 232 $[M-CF_2]^+$ (30), 213 $[M-CF_3]^+$ (100).

No arenes containing more than three trifluoromethyl groups were found in the products of the anodic trifluoromethylation of 3-trifluoromethylnitrobenzene.

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