Compounds (XVa) and (XVc) were similarly obtained (see Tables 1-3).

(Dichloromethyl)acetylmesitylene (I, X = $CHCl_2$, Y = Ac). To a solution of 1.0 g (5.20 mmoles) of acetylformylmesitylene (IIe) in 50 ml of CH_2Cl_2 was added 2.1 g (10.4 mmoles) of PCl_5 at 20°C with stirring. The reaction material was stirred for 2 h and poured into water, and the organic layer was separated and washed with water (3 × 50 ml). After the solvent was driven off and the residue was recrystallized from hexane, we obtained 0.92 g (72%) of compound (I, X = $CHCl_2$, Y = Ac) with mp 110-113°C. Found, %: C 58.75; H 5.87; Cl 28.38. $C_{12}H_{14}Cl_2O$. Calculated, %: C 58.79; H 5.57; Cl 28.92. PMR spectrum (δ, ppm): 2.60 (2-CH_3), 2.21 (4-CH_3), 2.50 (6-CH_3), 7.21 (-$CHCl_2$), 6.92 (H_{arom}).

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FLUORINATION OF ANIONIC σ-COMPLEXES BY CESIUM FLUOROXYSULFATE

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Anionic σ-complexes and related structures react with cesium fluoroxysulfate to give predominantly the C-fluoro derivatives: fluoronitrocyclohexadienes or substituted fluoronitrobenzenes. Oxidation or degradation of a complex to form substituted nitrobenzenes is also possible. The balance between all these processes is determined by the structure of the original complex.

The formation, stability, and structure of anionic σ-complexes (AC) have been the subject of numerous articles and reviews (see [1-3], for example). Less well studied are the reactions of AC with electrophiles, halogenation for example, and the related possibilities of using AC in synthesis [4, 5].

Unlike chlorination and bromination, fluorination of AC has not yet been studied. This is quite understandable in view of the lability of most AC and the corrosive nature of most electrophilic fluorinating agents.

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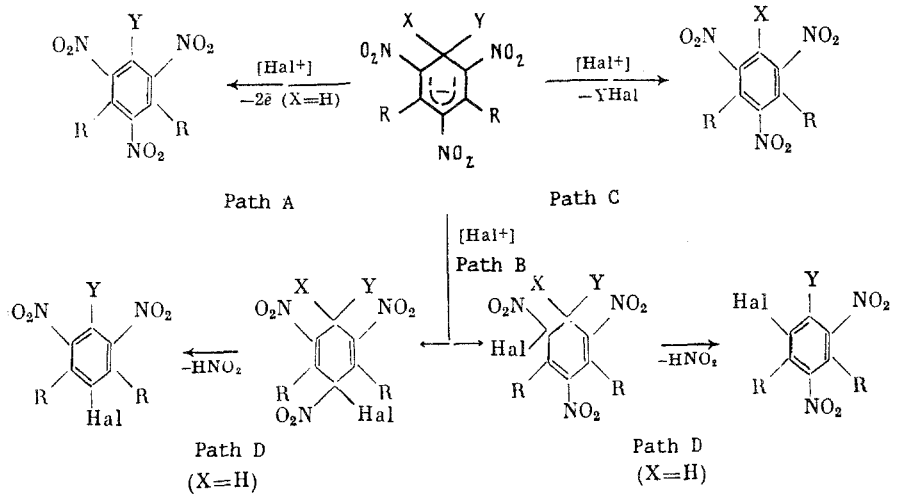
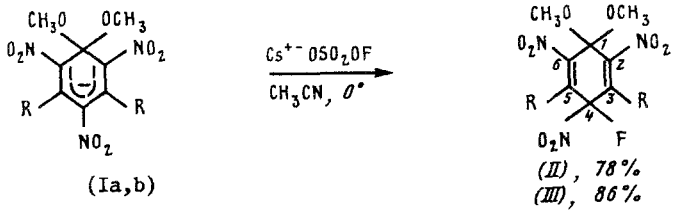
Typical processes which may occur during halogenation are shown in the following scheme.



As a rule, chlorination and bromination of AC results in their oxidation [4], i.e., the reaction proceeds via path A. In certain cases, however, C-halogenation products have been detected (path B) [5]. Considering the high energy of the C–F bond, it might be expected that, in the case of fluorination of AC, formation of C-fluorination products would be favored, and not oxidation, i.e., the reaction would proceed via path B. In order to rule out the possibility of oxidation of AC (path A) or subsequent elimination of HNO_2 (path D) from fluoronitrocyclohexadienes formed initially, we investigated first fluorination of the simplest stable σ-complexes of 2,4,6-trinitroanisole and sym-trimethoxytrinitrobenzene with potassium methylate.

We used cesium fluoroxysulfate (CFS) as a source of electrophilic fluorine; this is a unique ionic electrophilic fluorinating agent currently used for selective fluorination of unsaturated, aromatic, and heteroorganic compounds [6-8]. The reaction of CFS with AC represents a quite rare type in organic chemistry in that it is the interaction of an anion with an anion, which added additional interest to this process.

It has been established that CFS reacts with potassium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienoate (Ia) ($K_{stab} = 1.7 \cdot 10^4$ in MeOH [1]) in acetonitrile to give the expected product of C-fluorination (II) in good yield. Similarly, potassium 1,1,3,5-tetramethoxy-2,4,6-trinitrocyclohexadienoate (Ib) forms the correspnding fluoro derivative; in both cases the fluorination takes place predominantly at position 4:

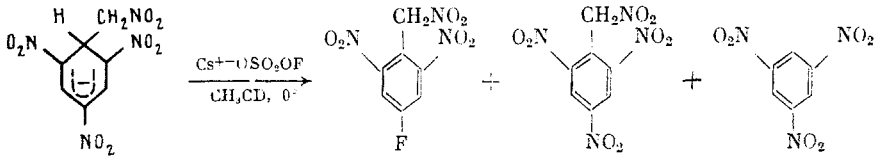


R = H (Ia), (II); OCH_3 (Ib), (III).

This regional selectivity of the process, in our opinion, may be due either to steric factors or to preliminary coordination of the reacting species.

Fluorination of AC based on 1,3,5-trinitrobenzene is more complex, since side processes are also possible (oxidation of the AC, HNO_2 elimination, and AC degradation). Thus, interaction of potassium 1-nitromethyl-2,4,6-trinitrocyclohexadienoate (Ic) with CFS in acetonitrile results in a mixture of products, from which the following were isolated by column chromatography: 1,3,5-trinitrobenzene, 1-nitromethyl-2,6-dinitro-4-fluorobenzene (IV), and 1-nitromethyl-2,4,6-trinitrobenzene (V) (see scheme on top of following page).

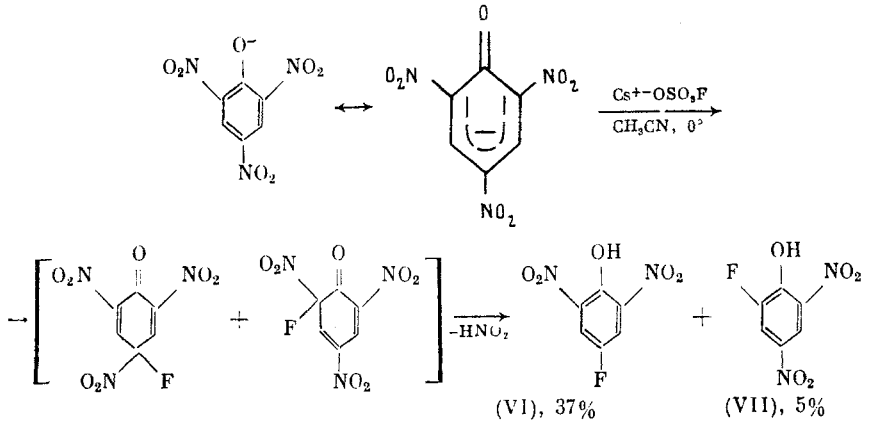
We associate the formation of the aromatic fluoro compound (IV) with elimination of the elements of HNO_2 from the initially formed product of C-fluorination of the AC (path D in the scheme).



(IV), 12% (V), 16% 22%

Anionic complexes of low stability, for example potassium 1-methoxy-2,4,6-trinitrocyclohexadienoate (Id) (K_{stab} = 17 [1]), are not fluorinated by CFS. The AC is degraded on reacting CFS with (Id) and 1,3,5-trinitrobenzene is recovered.

It should be noted that CFS is also able to fluorinate salts of picric acid. Here the formation of a mixture of 2- and 4-fluoronitrophenols may be explained within the framework of a common scheme for reaction of AC and analogous systems with CFS, consisting of intermediate formation of nonaromatic C-fluoronitrocyclohexadienones with subsequent elimination of HNO_2.



(VI), 37% (VII), 5%

The structure of the products was established by analysis of ^1H, ^{13}C, and ^{19}F NMR spectra and confirmed by elemental analysis. Although formation of molecular ions is not observed in mass spectra under electron-impact conditions, characteristic $M^+ - NO_2$ ions are always present in the spectrum.

Thus, reaction of AC and related structures with CFS gives predominantly C-fluorination products but may be complicated by subsequent elimination of the elements of HNO_2 or by oxidation of the AC. Similar processes have been observed during alkylation of certain AC, for example [9].

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were measured on a Bruker WM-250 spectrometer relative to TMS and $CFCl_3$, respectively; ^{13}C and ^{14}N NMR spectra were measured on a Bruker AM-300 instrument relative to TMS and internal $Me^{14}NO_2$ (weak-field shifts positive), respectively (see text for numbering of the atoms). Mass spectra were obtained in a Varian MAT CH-6 assembly (electron impact, 70 eV). The IR spectra were measured on a Specord IR-75 spectrometer using KBr pellets. Products were separated by column chromatography (3 × 20 cm) using silica gel L 40/100 from Chemapol (Czechoslovakia) as the sorbent. Cesium fluoroxysulfate (CFS) [7], trinitroanisole [10], and 1,3,5-trimethoxy-2,4,6-trinitrobenzene [11] were produced by well-known procedures.

1,1-Dimethoxy-4-fluoro-2,4,6-trinitrocyclohexadiene-2,5 (II). To a solution of 2.5 g (10 mmoles) of 2,4,6-trinitroanisole in 10 ml of abs. methanol at 0 to +5°C we added 12.5 ml 0.9 M MeOK solution dropwise with stirring and allowed it to stand for 15 min at the same temperature. To the resulting solution we added 30 ml of abs. ether, filtered the precipitate formed, and then washed it with a small amount of ether followed by drying. The precipitate obtained (Ia) was suspended in 30 ml abs. CH_3CN followed by addition of 3.0 g (12 mmoles) of CFS in small portions with stirring at 20°C over a period of 10 min (until the bright-red color was discharged). The resulting mixture was filtered and the precipitate washed on the filter with a small amount of ether. The filtrate was concentrated on a ro-

tary evaporator and the residue extracted three times with 30 ml portions of $CHCl_3$; the extract was washed three times with water, dried over $MgSO_4$, and the solvent removed on a rotary evaporator. Yield 2.3 g (76%) of (II), mp 92-93°C (CCl_4). Found, %: C 33.13; H 2.88; F 6.38; N 13.58. $C_8H_8FN_3O_8$. Calculated, %: C 32.76; H 2.73; F 6.48; N 14.33. PMR spectrum (δ, ppm; J, Hz; $CDCl_3$): 7.81 d.d (2H, H^3, $^3J_{H-F}$ = 6.0, $^3J_{H-H}$ = 2.3); 358 s (3H, OCH_3); 3.49 s (3H, OCH_3). ^{13}C NMR spectrum (δ, ppm; J, Hz; acetone-d_6): 153.21 d.d.d ($C^{2(6)}$, $^3J_{C-F}$ = 10.4, J_{C-H} = 9.9, 4.7); 126.32 d.d.d ($C^{3(5)}$, $^2J_{C-F}$ = 27.5, J_{C-H} = 180.5, 4.4); 108.63 d.t (C^4, $^1J_{C-H}$ = 234.0, J_{C-H} = 2.7); 96.77 m ($C^{1,4}J_{C-F}$ = 3.3, J_{C-H} = 5.2, 6.8); 54.24 q (OCH_3), 53.90 q (OCH_3). ^{14}N NMR spectrum (δ, ppm; $\Delta\nu_{1/2}$, Hz; acetone-d_6): −19.51 br.s (2N, C−NO_2, $\Delta\nu_{1/2}$ = 75); −8.23 (1N, $CFNO_2$, $\Delta\nu_{1/2}$ = 120). ^{19}F NMR spectrum (δ, ppm; acetone-d_6): −111.2 ($CFNO_2$). Mass spectrum (m/z): 216[M^+ − 46(NO_2) − 31(OCH_3)]; 201[M^+ − 92($2NO_2$)]. IR spectrum (ν, cm^{-1}): 692 s, 763, 791, 815, 858, 903, 917, 926, 958, 1064, 1096, 1120 v.s, 1168, 1221, 1271, 1293, 1336, 1350 v.s, 1460, 1546 v.s, 1592 s, 1668, 1684, 1705, 2850, 2950, 2980, 3020, 3078.

1,1,3,5-Tetramethoxy-4-fluoro-2,4,6-trinitrocyclohexadiene-2,5 (III). This was synthesized using the same procedure as for (II); 3.0 g (10 mmoles) of 1,3,5-trimethoxy-2,4,6-trinitrobenzene yielded 3.0 g (86%) of (III), mp 125-126°C (CCl_4). Found, %: C 34.69; H 3.50; F 5.26; N 11.94. $C_{10}H_{12}FN_3O_{10}$. Calculated, %: C 33.99; H 3.40; F 5.38; N 11.90. PMR spectrum (δ, ppm; J, Hz; $CDCl_3$): 4.05 d (6H, OCH_3, $^4J_{H-F}$ = 0.6); 3.64 s (3H, OCH_3); 3.54 s (3H, OCH_3). ^{13}C NMR spectrum (δ, ppm; J, Hz; $CDCl_3$): 143.14 d.q ($C^{3(5)}$, $^3J_{C-F}$ = 20.3, J_{C-H} = 4.2); 130.38 d ($C^{2(6)}$, $^3J_{C-F}$ = 4.7); 107.74 d (C^4, $^1J_{C-F}$ = 249.7); 99.70 d.d (C^1, $^4J_{C-F}$ = 2.3, J_{C-H} = 4.2); 60.66 q (OCH_3); 53.77 q (OCH_3); 53.07 q (OCH_3). ^{14}N NMR spectrum (δ, ppm: $\Delta\nu_{1/2}$, Hz; $CDCl_3$): −22.56 (1N, $CFNO_2$, $\Delta\nu_{1/2}$ = 100); −16.37 (2N, C−NO_2, $\Delta\nu_{1/2}$ = 140). ^{19}F NMR spectrum (δ, ppm; $CDCl_3$); −121.6 ($CFNO_2$). Mass spectrum (m/z): 216[M^+ − 46(NO_2) − 31(OCH_3)]; 201[M^+ − 92($2NO_2$)]. IR spectrum (ν, cm^{-1}): 728 s, 761, 813, 854 s, 943, 987, 1041, 1087 s, 1138 v.s, 1187, 1222, 1281 s, 1344, 1363, 1443, 1458, 1537 s, 1550 v.s, 1607 v.s, 1676, 1704, 2845, 2945.

Interaction of Potassium 1-Nitromethyl-2,4,6-trinitrocyclohexadienoate (Ic) with CFS. To a mixture of 2.0 g (9.4 mmoles) of 1,3,5-trinitrobenzene, 5 ml of nitromethane, and 5 ml abs. MeOH at 0°C was added 11 ml 0.9 M MeOK solution dropwise with stirring and allowed to stand for 20 min at the same temperature. The reaction mass was diluted with 50 ml of dry ether, the precipitate of (Ic) filtered, washed with ether on the filter, dried for a short time in air, and suspended in 10 ml abs. CH_3CN. To the resulting mixture at 0°C and with stirring we added in small portions 2.7 g (1.1 mmoles) of CFS (until the bright-red color was discharged). The reaction mixture was filtered and the precipitate washed on the filter with a small amount of ether. The combined filtrates were evaporated on a rotary evaporator and the residue chromatographed (hexane–ether = 10:1 → 3:1 eluant). Yield 0.3 g (16%) of (IV), 0.2 g (12%) of (V), and 0.4 g (20%) of 1,3,5-trinitrobenzene. Melting point of (IV) 91-92°C. Found, %: C 34.81; H 1.76; F 7.62; N 16.87. $C_7H_4FN_3O_6$. Calculated, %: C 34.29; H 1.63; F 7.76; N 17.14. PMR spectrum (δ, ppm; J, Hz; DMSO-d_6): 8.22 d (2H, $H^{3(5)}$, $^3J_{H-F}$ = 7.3); 5.96 s (2H, CH_2NO_2). ^{19}F NMR spectrum (δ, ppm; DMSO-d_6): −101.4 t (C−F, $^3J_{F-H}$ = 7.4). Mass spectrum (m/z): 199[M^+ − 46(NO_2)]; 151[M^+ − 94($2HNO_2$)]. Melting point of (V) 114-115°C. PMR spectrum (δ, ppm; J, Hz; DMSO-d_6): 9.1 s (2H, $H^{3(5)}$); 6.2 s (2H, CH_2NO_2) (cf. [12]: mp 114-116°C; PMR spectrum (δ, ppm; acetone-d_6): 9.24 s (2H, $H^{3(5)}$); 6.3 s (2H, CH_2NO_2); mass spectrum (m/z): 226[M^+ − 46(NO_2)]).

Interaction of Sodium Picrate with CFS. To a suspension of 1.5 g (6 mmoles) of sodium picrate in 15 ml abs. CH_3CN at 20°C with stirring we added by portions 1.8 g (7.8 mmoles) of CFS and kept it at the same temperature for 1 h with stirring. The reaction mass was filtered and the precipitate washed on the filter with a small amount of CH_3CN. The combined filtrates were evaporated on a rotary evaporator and the residue separated chromatographically with $CHCl_3$ as eluant. Yield 0.5 g (42%) (calculated on the basis of picric acid reacted) of a 7:1 mixture of (VI) and (VII), together with 0.4 g (29%) of picric acid. PMR spectrum of (VI) (δ, ppm; J, Hz; $CDCl_3$): 11.2 br.s (1H, OH); 8.13 d (2H, $H^{3(5)}$, $^3J_{H-F}$ = 6.9). ^{19}F NMR spectrum (δ, ppm; J, Hz; $CDCl_3$): −125.3 t (C−F, $^3J_{F-H}$ = 7.0). Mass spectrum (m/z): 202[M^+]. (cf. [13]: mp of (VI) 49-50°C.) Melting point of (VII) 100-102°C. PMR spectrum (δ, ppm; J, Hz; $CDCl_3$): 11.2 br.s (1H, OH); 8.89 d.d (1H, H^5, $^1J_{H-H}$ = 3.0, $^5J_{H-F}$ = 2.1); 8.32 d.d (1H, H^3, $^4J_{H-H}$ = 3.0, $^3J_{H-F}$ = 9.5). ^{19}F NMR spectrum (δ, ppm; J, Hz; $CDCl_3$): −118.4 d.d (C−F, $^3J_{F-H}$ = 9.4, $^5J_{F-H}$ = 2.0). Mass spectrum (m/z): 202[M^+]. (cf. [14]: mp of (VII) 101-102°C.)

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REACTIONS OF POLYFLUOROALKYLSULFENYL CHLORIDES WITH PHENOLS

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Polyfluoroalkylsulfenyl chlorides thiolate phenol and its ortho- and meta-substituted derivatives regiospecifically at the para-position in the absence of a catalyst and of a hydrogen chloride acceptor. Ortho thiolation occurs with significantly greater difficulty in the para-substituted phenols, and is only possible with the strong electron-donor properties of the substituent. Polyfluoroalkylthiolation of phenols is rendered more difficult with the increase in the steric impediments at the sulfur atom of the sulfenyl chloride and the volume of the substituents by the OH group of the phenol.

It was previously shown [1] that 1-trifluoromethyl-2-chloroethylsulfenyl chloride, in contrast to trifluoromethyl- and perfluoroheptylsulfenyl chlorides [2-4], interacts with phenols in the absence of a catalyst or an HCl acceptor. The thiolation thereby occurs selectively at the para- and ortho-position depending on the nature of the solvent. The present communication investigates the features of the noncatalyzed thiolation of phenol and its derivatives with 2-chlorotetrafluoroethyl-, 2,2-dichlorotrifluoroethyl-, and α-methoxycarbonylhexafluoroisopropylsulfenyl chloride (I)-(III), respectively.

The interaction of the sulfenyl chlorides (I)-(III) with phenol occurs regiospecifically at the para-position at 20°C with the formation of the phenols (IV)-(VI), and is independent of the nature of the solvent utilized. The time for the completion of the reaction increases with the increase in the steric hindrance at the sulfur atom (see scheme on page 1438).

The ortho-substituted phenols are thiolated by (I)-(III) exclusively at the para-position giving the derivatives (VII)-(X). In this case, steric impediments at the hydroxyl

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