Cation Radicals. 47. Reaction of Perylene Cation Radical with Fluoride Ion and of Perylene with Xenon Difluoride. Formation of 1-Fluoro-, 3-Fluoro-, and a Difluoroperylene. Complications with Chloride Ion Impurity[1,2]

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Proposals that anodic[3] and metal fluoride[4] fluorinations of aromatics involve reactions of aromatic cation radicals with fluoride ion are to be found in the literature. In contrast, successful reactions of isolated cation radicals with fluoride ion had never been reported until recently.[5] At that time it was found by mass spectrometry that when perylene cation radical perchlorate ($1^{+\cdot}$,ClO_4^-) reacted with fluoride ion a small amount of a fluoroperylene was present in the almost quantitatively formed major product, perylene (1). We now show that, in fact, both 1-fluoro- (2) and 3-fluoroperylene (3) are formed, as well as a difluoroperylene (4). The major product is again 1, and we now attribute its formation to reduction of $1^{+\cdot}$ by the conjugate base of the solvent, acetonitrile. We find also that reaction of $1^{+\cdot}$ occurs competitively with small amounts of chloride ion which may be present as an impurity or which are formed from solvent methylene chloride. These observations help to clarify some confusion over cation radical–fluoride ion reactions and have a bearing on not only cation radical–halide ion reactions but also on synthesis of fluoroaromatics by reaction of arenes with xenon fluoride.
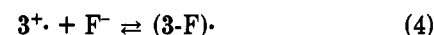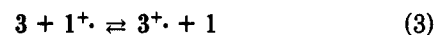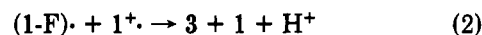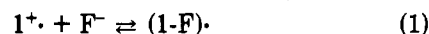
Crystalline $1^{+\cdot}$,ClO_4^- was prepared by anodic oxidation of 1 in methylene chloride. Reaction with tetraethylammonium fluoride (TEAF) in acetonitrile gave 89% perylene and an inseparable mixture of fluoro-, chloro-, difluoro-, and chlorofluoroperylene, all of which were identified in the mixture by high-resolution mass spectrometry. The fluoroperylene has been found, by comparing ^{19}F FT NMR spectra of the mixture with those of authentic compounds, to be, in fact, both 1-fluoro- (2) and 3-fluoroperylene (3), the latter being predominant. The source of the chlorine atom in some of the products was found to be twofold: from the cathodic decomposition of methylene chloride in the preparation of $1^{+\cdot}$,ClO_4^-, and as a small impurity in the TEAF. That is, when $1^{+\cdot}$,ClO_4^-, prepared by oxidation of 1 in methylene chloride, was isolated and reduced by iodide ion the expected product (1) was found by mass spectrometry to contain chloroperylene. The cathode compartment of the three-compartment cell was found to contain chloride ion. Apparently, chloride ion diffused into the anode compartment and the isolated $1^{+\cdot}$,ClO_4^- contained some chloroperylene

cation radical perchlorate. To avoid this problem $1^{+\cdot}$,BF_4^- was prepared by oxidation of 1 in tetrahydrofuran[5] and was found to be free of chloroperylene. Reaction of $1^{+\cdot}$,BF_4^- with TEAF in acetonitrile gave again, however, fluoro- and difluoroperylenes contaminated with chloro- and chlorofluoroperylene. Attempts to purify TEAF failed and led to further complications.[6] The interference of small amounts of chloride ion in the reactions of $1^{+\cdot}$ with fluoride ion results from the much greater reactivity of chloride than fluoride in reactions with cation radicals.[12]

A common way of making fluoroaromatics is by reaction of the arene with xenon difluoride in methylene chloride. When this was tried with perylene the formation of $1^{+\cdot}$ was observed spectrophotometrically and the same problem with products was encountered; that is, a mixture of fluoro-, difluoro-, chloro-, and chlorofluoroperylene was obtained. Apparently, fluoride ion formed in this reaction caused elimination of chloride ion from the solvent, and the chloride competed with fluoride ion in reaction with $1^{+\cdot}$.[14] Finally, successful fluorination of perylene was achieved with xenon fluoride in perfluorohexane, when 3 and a difluoroperylene were obtained. These were not separated on a preparative scale, but were characterized by TLC, HPLC, and mass spectrometry.

It seems to us now that the difficulty in achieving successful nucleophilic reactions of fluoride ion with isolated perylene and analogous cation radicals[17] is caused by the extremely low nucleophilicity but high basicity of the fluoride ion. The major product from reaction of $1^{+\cdot}$ is 1 itself. Yet, fluoride ion cannot be the reducing agent. We attribute the reduction to the solvent anion, $NCCH_2^-$, believed to be formed by deprotonation of the solvent.[18] We have tried but failed to discover the fate of the reducing agent (i.e., by looking for succinonitrile). Fluoride ion is so poorly nucleophilic that even very low concentrations of chloride ion compete successfully with it and lead, in fact, to complications not only in our direct reactions with $1^{+\cdot}$ but also in the xenon fluoride reactions.

The formation of 4 shows that electron exchange between $1^{+\cdot}$ and 3 undoubtedly occurs after 3 has been formed (eq 1-5). Reactions of this kind may account for

$$1^{+\cdot} + F^- \rightleftarrows (1\text{-}F)\cdot \tag{1}$$

$$(1\text{-}F)\cdot + 1^{+\cdot} \rightarrow 3 + 1 + H^+ \tag{2}$$

$$3 + 1^{+\cdot} \rightleftarrows 3^{+\cdot} + 1 \tag{3}$$

$$3^{+\cdot} + F^- \rightleftarrows (3\text{-}F)\cdot \tag{4}$$

(6) TEAF is used in aprotic solvents as a source of strongly basic fluoride ion.[7-11] The melting point reported by Hayami is 110 °C.[8] We found that Eastman's dihydrate had mp 110 °C and contained small amounts of chloride ion. Crystallization from acetonitrile gave mp 191 °C, and chloride ion was still present. Crystallization from ethanol gave a product with mp >360 °C and which no longer corresponded analytically with TEAF.

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(18) The deprotonation of acetonitrile by fluoride ion, leading to Michael additions of $NCCH_2^-$, has been reported by Rozhkov.[19]

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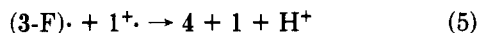
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$$(3\text{-}F)\cdot + 1^{+}\cdot \rightarrow 4 + 1 + H^{+} \qquad (5)$$

the reported formation of other dihalogen aromatics in cation radical–halide ion reactions.[17]

Experimental Section

Materials. Perylene (Sigma Chemical Co.) was purified by column chromatography on silica with benzene elution and was then crystallized from benzene, mp 284–285 °C. The product gave a single spot on TLC and an acceptable mass spectrum. Electrolytes tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium tetrafluoroborate (TBAT) were electrometric grade from Southwestern Analytical Chemicals. Each was ground and dried under vacuum at room temperature to a free-flowing powder. Tetraethylammonium fluoride (TEAF) from Eastman was similarly treated immediately before use. Xenon difluoride and perfluorohexane were both from PCR Research Chemicals and were used as obtained. Methylene chloride was refluxed over calcium hydride for 1 h and fractionally distilled. Tetrahydrofuran (THF) was refluxed for 3 h over lithium aluminum hydride and fractionally distilled under N_2. Acetonitrile for cation radical reactions was Eastman's anhydrous grade (0.05% water) and was used as obtained, stored over molecular sieves. Silica gel for column chromatography was Woelm No. 402809, 0.2–0.5-mm particle size. Silica gel for TLC was Woelm No. 404680, containing a fluorescent indicator.

Preparation of 3-Fluoroperylene by the Balz–Schiemann Reaction. 3-Nitroperylene was prepared by the reaction of perylene cation radical with nitrite ion[20] and was reduced to 3-aminoperylene with hydrazine and palladium.[21] Diazotization and the Balz–Schiemann reaction were carried out essentially by the procedure of Lund and Berg.[22] A solution of 100 mg (0.38 mmol) of 3-aminoperylene in 100 mL of acetic acid was poured into 100 mL of 2.2 N sulfuric acid. The precipitated salt was suspended in 150 mL of 2 N sulfuric acid at 10 °C. To this was added dropwise 2 mL of 6% sodium nitrite solution, and after 1 h of stirring 5 mL of 49% fluoroboric acid was added to the dark purple solution. After a further 1 h of stirring the solution was filtered. The dark, washed and dried solid was crushed and boiled in xylene for 30 min. The solvent was removed in a rotary evaporator, giving 68 mg of product. This was dissolved in 20 mL of methylene chloride and used for TLC on silica (116 plates), giving 40 mg (59%) of 3-fluoroperylene, 24.6 mg of 3-aminoperylene, and 3 mg of perylene.

The 3-fluoroperylene was crystallized from benzene–petroleum ether and had mp 238–239 °C. Mass spectrometry showed no sign of chloroperylene in the product: calcd for $C_{20}H_{11}F$ 270.08447, found 270.0843.[23] ^{19}F FT NMR in naphthalene at 90 °C: δ (vs. $CFCl_3$) 119.2 (dd, J = 5.4, 10.0 Hz).[24] UV (CH_2Cl_2) λ_{max} (10^{-4} ε): 250 (sh, 1.88), 256 (2.26), 390 (0.75), 413 (1.56), 439 (1.95). $E_{1/2}$ = 0.705 V at a Pt anode in CH_3CN vs. Ag/Ag^+ 0.1 M in CH_3CN.

When 3-aminoperylene was precipitated as its hydrochloride from acetic acid and diazotization and preparation of the diazonium tetrafluoroborate were carried out in 6 N hydrochloric acid, 3-fluoroperylene was obtained which contained 1.7% chloroperylene.[23]

Preparation of 1-Fluoroperylene. 1-Nitroperylene,[25] made by Looker's method,[26] was reduced to 1-aminoperylene, mp 195–196 °C.[26] The 1-aminoperylene (142 mg, 0.53 mmol) was converted into its acid sulfate salt and diazotized as described above. Diazotization gave a black solution, and addition of fluoroboric gave a black solid. This was heated in boiling xylene and the filtered xylene solution gave 57 mg of solid after removal of the xylene. The solid was dissolved in benzene and the solution was used for TLC and HPLC to give 11 mg of 1-fluoroperylene,

mp 158–160 °C. This was not recrystallized but was used for ^{19}F FT NMR in naphthalene at 90 °C. A peak with δ (vs. $CFCl_3$) 106 was obtained. This gave a broad partially resolved spectrum after 41000 scans; a well-resolved spectrum could not be achieved.[24]

Reaction of Perylene Cation Radical Perchlorate with Fluoride Ion. A. Preparation in Methylene Chloride. Formation of Chloro- and Fluoroperylenes. Perylene (500 mg, 1.98 mmol) in 300 mL of 0.1 M TBAP in methylene chloride was oxidized at 1.4 V vs. a silver wire quasi reference electrode. $1^{+}\cdot,ClO_4^{-}$ began depositing on the cylindrical platinum sheet anode as soon as current was applied. After 115 coulombs (60% of the current for one-electron oxidation) had passed the oxidation was stopped. The anode was washed with methylene chloride, and the deposit was carefully scraped off with a porcelain spatula and dried under vacuum to give 526 mg (1.44 mmol, 73%) of product. Iodometric assay gave 96% cation radical content. The major portion (483 mg, 1.32 mmol) was added to 1 L of acetonitrile containing 304 mg (2.04 mmol) of TEAF. The color of $1^{+}\cdot$ dissipated within a few minutes. The solvent was evaporated, and the residue was washed with water, dried, and passed through a short column of Woelm neutral alumina (No. 402135) (benzene elution) to give 355 mg of solid. Extensive separation by TLC gave 298 mg (1.18 mmol) of perylene, 43 mg of what appeared from TLC to be 3-fluoroperylene, and 13.6 mg of what appeared to be difluoroperylene. High-resolution mass spectrometry showed, however, that the larger fraction was a mixture of fluoroperylene (m/e 270.0843, calcd 270.08447), chloroperylene (m/e 286.05492, 288.05197, calcd 286.05532, 288.05228), difluoroperylene (m/e 288.07473, calcd 288.07504), and chlorofluoroperylene (m/e 304.04519, calcd 304.04549, second peak observed but not matched).[23] HPLC separated these compounds and showed that the fluoro- and chloroperylene predominated, but no attempt was made to isolate the individual components of the mixture. Also, ^{19}F FT NMR showed that two monofluoroperylenes were present, 3-fluoroperylene predominantly and a small amount of 1-fluoroperylene.[24] The two isomers were identified by chemical shift (119.2 and 106 ppm, respectively), using authentic compounds, while the 3-fluoroperylene was also identified by coupling constants (J = 5.4, 10.0 Hz). Resolution of the 1-fluoroperylene spectrum could not be achieved. The smaller TLC fraction (13.6 mg) was shown by mass spectrometry to be mainly a difluoroperylene containing small amounts of chloro-, chlorofluoro-, and dichloroperylene.

The source of chlorine in the products was shown to be both from the solvent methylene chloride and the TEAF. Thus, oxidation of perylene in methylene chloride containing tetrabutylammonium tetrafluoroborate (TBAT) as electrolyte gave a product presumed to be $1^{+}\cdot,BF_4^{-}$. When this was reduced with potassium iodide in acetonitrile, however, the product was found by mass spectrometry to be perylene containing some chloroperylene (m/e 286, 288). Chloride ion was found to be present in the water extract of the catholyte, although none was found in the extract of the anolyte.

B. Preparation in THF. Similar oxidation of perylene in THF containing TBAT gave $1^{+}\cdot,BF_4^{-}$, a sample of which was reduced with potassium iodide and gave perylene only. The $1^{+}\cdot,BF_4^{-}$ reacted with TEAF (contaminated with chloride ion) in acetonitrile and gave a product which again proved by mass spectrometry and HPLC to be a mixture of fluoro-, difluoro-, chloro-, and chlorofluoroperylene.

Reaction of Perylene with XeF_2. A. In Methylene Chloride. XeF_2 (138 mg, 0.82 mmol) was placed in a polyethylene bottle and cooled in liquid N_2 in a drybox. To the bottle was added slowly a solution of 181 mg (0.72 mmol) of perylene in 100 mL of methylene chloride. The mixture was allowed to warm up to room temperature, after which it was removed from the drybox and stirred. After 3.5 h the homogeneous solution had the visible spectrum of the perylene cation radical. After 30 h the solution was washed with aqueous potassium carbonate, dried, and evaporated. The product (201 mg) was separated by TLC (132 plates) into three fractions. These were found, however, by mass spectrometry and HPLC to be mixtures containing chlorinated perylene. The first TLC band (highest R_f, not measured) contained mostly a chlorofluoroperylene (m/e 304, 306) and small amounts of perylene and fluoro- and difluoroperylene. The second band (R_f 0.15) was mostly 3-fluoroperylene with small amounts

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(24) We thank Dr. Ben Shoulders, University of Texas, Austin, TX, for considerable help with the ^{19}F FT NMR.
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of perylene and chloro-, difluoro-, and chlorofluoroperylene, while the last band was perylene containing small amounts of fluoro- and chlorofluoroperylene.

B. In Perfluorohexane. The same procedure was used with 158 mg (0.63 mmol) of perylene suspended in 50 mL of perfluorohexane and 257 mg (1.52 mmol) of XeF_2. However, neither of these compounds is very soluble in the perfluorohexane so that after removal from the drybox the mixture was agitated periodically during 48 h. Reaction occurred on the surface of the perylene which became blackened. The suspension was shaken with aqueous sodium carbonate and filtered to give 177 mg of solid. This was dissolved in 100 mL of benzene and 10 mL of the solution was used for TLC (91 plates). Separation gave the crude products (in band order) as a difluoroperylene (10%), 3-fluoroperylene (30%), and perylene (60%). Each of the fluoro compounds was found by HPLC to contain very small amounts of the other products. The disposition of HPLC peaks was such that purification of the 3-fluoro- and difluoroperylene by recycling and preparative HPLC would have been possible but tedious and this was not attempted.

Registry No. 1, 198-55-0; 1$^+$·, ClO$_4^-$, 12576-63-5; 2, 77629-23-3; 3, 77647-88-2; 4, 77647-95-1; F$^-$, 16984-48-8; XeF$_2$, 13709-36-9.

Trifluoroacetic Acid Catalyzed Rearrangement of Dialkyl Xanthates to Dithiocarbonates with Inversion of Configuration

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The thermal rearrangement of alkyl xanthates to *S,S*-dialkyl dithiocarbonates has long been known, usually occurring when the xanthates have no β hydrogen[1] or as a side reaction in the normal olefin formation during the Chugaev reaction. More recently, this rearrangement of xanthate to dithiocarbonate has been found to be catalyzed by Lewis acids, although side products are also observed.[2] The ready conversion of xanthates and *S,S*-dialkyl dithiocarbonates to thiols upon treatment with 2-aminoethanol or ethylenediamine can offer an attractive synthesis of mercaptans from alcohols,[4] particularly, if optically active thiols can be formed.[5] During our work on the synthesis of 1,3-dithiol-2-ones via xanthate intermediates, we discovered that trifluoroacetic acid catalyzed the rearrangement of dialkyl xanthates to *S,S*-dialkyl dithiocarbonates in high yields and under mild conditions. The rearrangement occurred without evidence of olefin formation even with xanthates with a β hydrogen on the oxygen alkyl group.

Results and Discussion

Recently, the mechanism of the Lewis acid catalyzed rearrangement of dialkyl xanthates to *S,S*-dialkyl dithio-

Scheme I

Scheme II
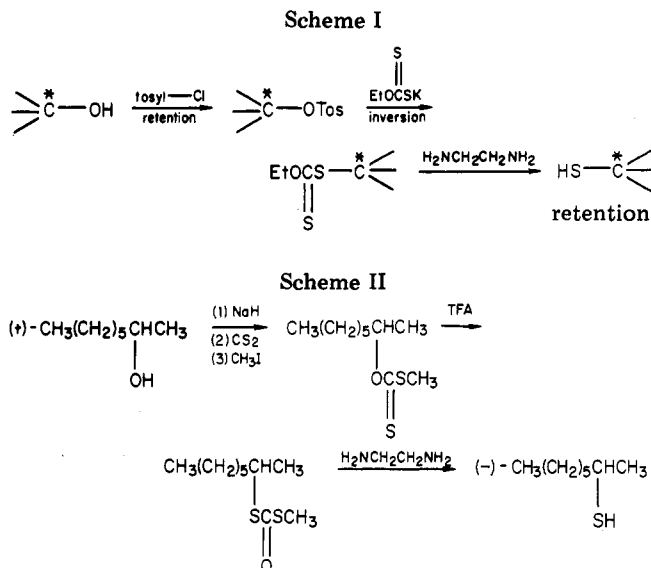
carbonates has been investigated.[3] The rate constants for the rearrangement of several *O*-alkyl *S*-methyl xanthates increased in the order Me, Et, *n*-Pr < *i*-Pr. In addition, the catalysis racemized the rearranged products derived from optically active alcohols. Both of these results are consistent with a carbenium ion intermediate. In our method for the same transformation, the *O*-alkyl *S*-methyl xanthate is stirred in trifluoroacetic acid at room temperature. Table I summarizes the synthetic data for the dithiocarbonates that were prepared. The progress of the conversion is nicely followed by NMR spectroscopy by observing the upfield shift for the *O*-alkyl to *S*-alkyl multiplets. This method also allows a convenient comparison of reaction rates. The rates of the rearrangement of *O*-alkyl *S*-methyl xanthates varied in the order Me > Et > *i*-Pr. For comparison, when the *O*-alkyl group was methyl, the transformation was 88% complete after 5 min at room temperature. With an *O*-ethyl group, the rearrangement was only 35% complete after 30 min and only 75% complete after 2 h at room temperature.[6] These results suggest that the mechanism for the trifluoroacetic acid catalyzed rearrangement differs from that observed for the Lewis acid catalyzed reaction.[3] To examine this difference more thoroughly, we prepared the *S*-methyl xanthate derived from (+)-2-octanol and subjected it to the rearrangement conditions. The derived *S*-methyl *S*-octyl dithiocarbonate was optically active (see Table II). There was no direct way to assess the stereospecificity of the rearrangement, because optical rotation data for this compound had not been reported. We determined the stereospecificity as follows. It has been demonstrated that a given optically active alcohol can be converted to the corresponding thiol in a sequence of steps in which inversion can occur at one of the steps only. The sign of the optical rotation of the mercaptan so obtained is opposite to that of the starting alcohol[4] (Scheme I). This information provides a convenient method for assessing the significance of the magnitude and sign of the optical activity obtained in the formation of the *S*-methyl *S*-(2-octyl) dithiocarbonate. By converting this material to the corresponding thiol with ethylenediamine and comparing its optical rotation with that from the thiol obtained via Scheme I, we would have an indication of the degree of inversion, retention, or racemization about the secondary

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(6) Reaction times can be decreased without ill effects by warming the reaction at 55–60 °C.