Table I. ^{13}C Chemical Shifts of Tetracycles 10, 11, 14, and 15[a]

	10[b]	11[b]	14a[c]	15a[c]	14b[c]	15b[c]
C(1)	38.3	39.2	37.8	37.9	37.7	37.8
C(2)	18.4	18.8	23.3	23.3	23.3	23.5
C(3)	36.5	36.6	79.7	79.6	79.6	79.8
C(4)	47.2	47.3	40.7	40.7	40.7	40.9
C(5)	49.6	49.6	54.7[d]	54.6	54.6	54.7[d]
C(6)	23.3	23.2	21.3	21.1	21.3	21.1
C(7)	39.8	39.8	40.4	40.4	39.7	40.0
C(8)	84.2	84.3	83.8	83.4	86.2	86.1
C(9)	54.8	55.1	54.4[d]	54.6	53.9	54.4[d]
C(10)	37.9	38.1	38.1	38.1	38.1	38.4
C(11)	17.4	17.5	18.7	19.0	18.7	18.4
C(12)	39.0	32.3	38.1	32.1	37.5	32.8
C(13)	41.9	41.6	41.8	41.4	44.8	44.6
C(14)	44.6	47.6	44.2	47.1	43.2	47.5
C(15)	82.0	85.3	82.0	85.2	81.3	82.2
C(16)	64.1	61.7	64.0	61.3	176.1	173.5
C(17)	20.4	23.2	20.3	23.0	21.7	24.0
C(18)	178.6	178.8	22.6	22.5	22.6	22.8
C(19)	17.1	17.2	64.9	64.9	65.0	65.2
C(20)	16.1	16.1	16.5	16.5	16.5	16.5

[a] In parts per million downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm. [b] $\delta(OMe) = 51.7$ ppm. [c] Acetate $\delta(CO) = 170.3 \pm 0.4$ ppm and $\delta(Me) = 20.9 \pm 0.1$ ppm. [d] Signals in any vertical column may be interchanged.

Methyl 16-Hydroxy-8α,15(*S*)-oxy-8,14,15,16-tetrahydrosandaracopimarate (10). A solution of 200 mg of diol **8** in 100 mL of dry chloroform was saturated with hydrogen chloride gas and kept at room temperature for 48 h. It was mixed with 100 mL of water and the organic solution washed with a saturated sodium bicarbonate solution and with water and dried (Na_2SO_4). It then was evaporated and the residue chromatographed on silica gel. Elution with 32:1 chloroform–methanol led to the recovery of 65 mg of starting diol and 110 mg of semisolid alcohol **10**; ^1H NMR δ 0.98, 1.00, 1.15 (s, 3 each, 3 Me), 3.2–3.7 (m, 3, OCH, OCH_2), 3.63 (s, 3, OMe).

Anal. Calcd for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78. Found: C, 71.78; H, 9.95.

Methyl 16-Hydroxy-8α,15(*R*)-oxy-8,14,15,16-tetrahydrosandaracopimarate (11). The same hydrogen chloride treatment of a solution of 200 mg of diol **9** in 100 mL of dry chloroform led to the recovery of 50 mg of starting diol and 100 mg of semisolid alcohol **11**; ^1H NMR δ 0.95, 1.02, 1.18 (s, 3 each, 3 Me), 3.3–3.8 (m, 3, OCH, OCH_2), 3.62 (s, 3, OMe).

Anal. Calcd for $C_{21}H_{34}O_4$: C, 71.96; H, 9.78. Found: C, 71.82; H, 9.89.

16-Hydroxy-8α,15ζ-oxy-7,8,15,16-tetrahydrovirescenol B Diacetate (14a and 15a). The identical treatment of a solution of 1.20 g of the diol **12** and **13** mixture[3] in 200 mL of dry chloroform yielded 1.20 g of crude alcohols, whose chromatography on silica gel and elution with 200:1 chloroform–methanol gave first crystalline C(15) *S* alcohol **14a**: mp 172 °C; ^1H NMR δ 0.98, 1.00, 1.01 (s, 3 each, 3 Me), 1.98, 2.00 (s, 3 each, 2 Ac Me), 3.2–3.8 (m, 3, OCH, OCH_2), 4.13 (4-line AB, 2, J = ca. 11 Hz, $AcOCH_2$), 4.50 (t, 1, J = 8 Hz, AcOCH).

Anal. Calcd for $C_{24}H_{38}O_6$: C, 68.22; H, 9.07. Found: C, 68.18; H, 9.40.

Further elution yielded crystaline C(15) *R* alcohol **15a**; mp 175–176 °C; ^1H NMR δ 0.97, 1.05, 1.05 (s, 3 each, 3 Me), 2.00, 2.01 (s, 3 each, 2 Ac Me), 3.4–3.8 (m, 3, OCH, OCH_2), 4.12 (4-line AB, 2, J = ca. 11 Hz, $AcOCH_2$), 4.50 (t, 1, J = 8 Hz, AcOCH).

Anal. Calcd for $C_{24}H_{38}O_6$: C, 68.22; H, 9.07. Found: C, 68.12; H, 9.37.

Jones Oxidation of Alcohols 14a and 15a. A solution of 1.0 mmol of Jones reagent (prepared from a solution of 70 g of chromium trioxide in 500 mL of water and 61 mL of concentrated sulfuric acid) was added slowly to a stirred solution of 290 mg of alcohol **14a** in 50 mL of acetone at 0 °C. After 0.5 h the mixture was decomposed with 5% sodium bisulfite solution, diluted with 150 mL of water, and extracted exhaustively with ether. The extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue over silica gel and elution with 200:1 chloroform–methanol gave 60 mg of starting material. Elution with 20:1 chloroform–methanol afforded 150 mg of semisolid acid **14b**; ^1H NMR δ 0.98, 1.05, 1.08 (s, 3 each, 3 Me), 2.01, 2.05 (s, 3 each, 2 Ac Me), 4.10 (s, 1, H-15), 4.18 (4-line AB, 2, J = ca. 11 Hz, OCH_2), 4.50 (t, 1, J = 8 Hz, OCH).

Anal. Calcd for $C_{24}H_{36}O_7$: C, 66.03; H, 8.31. Found: C, 66.21; H, 8.20.

A solution of 250 mg of alcohol **15a** in 40 mL of acetone was treated with 0.90 mmol of Jones reagent as above. Elution of the chromatography column with chloroform yielded 90 mg of semisolid lactone **16**: IR 1770 (s, C=O), 1730 (s, C=O) cm^{-1}; ^1H NMR δ 1.05, 1.05, 1.18 (s, 3 each, 3 Me), 2.03, 2.06 (s, 3 each, 2 Ac Me), 4.23 (4-line AB, 2, J = ca. 11 Hz, OCH_2), 4.50 (t, 1, J = 8 Hz, OCH).

Anal. Calcd for $C_{23}H_{34}O_6$: C, 67.95; H, 8.43. Found: C, 68.21; H, 8.36.

Elution with 200:1 chloroform–methanol gave 30 mg of starting alcohol and elution with 20:1 chloroform–methanol led to 100 mg of semisolid acid **15b**; ^1H NMR δ 0.93, 0.97, 1.00 (s, 3 each, 3 Me), 1.96, 1.98 (s, 3 each, 2 Me), 4.08 (s, 1, H-15), 4.20 (4-line AB, 2, J = ca. 11 Hz, OCH_2), 4.55 (t, 1, J = 8 Hz, OCH).

Anal. Calcd for $C_{24}H_{36}O_7$: C, 66.03; H, 8.31. Found: C, 65.91; H, 8.56.

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Registry No. 6, 1686-54-0; **8**, 77494-88-3; **9**, 77549-65-6; **10**, 77494-89-4; **11**, 77549-66-7; **12**, 72478-93-4; **13**, 72478-94-5; **14a**, 77494-90-7; **14b**, 77494-91-8; **15a**, 77549-67-8; **15b**, 77549-68-9; **16**, 77494-92-9.

A Short Route to Pyrenophorin and Vermiculine

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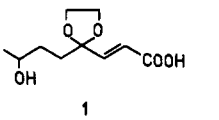
We report a new synthesis, from a common intermediate, of the monomeric units **1** and **2**, which correspond (and have been converted) to the dimeric macrolide (dilide) antibiotics (±)-pyrenophorin[2] (**3**) and (±)-vermiculine[3] (**4**).



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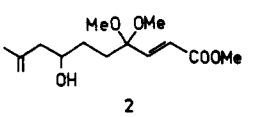

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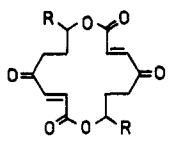

3 R = CH_3

4 R = CH_2COCH_3

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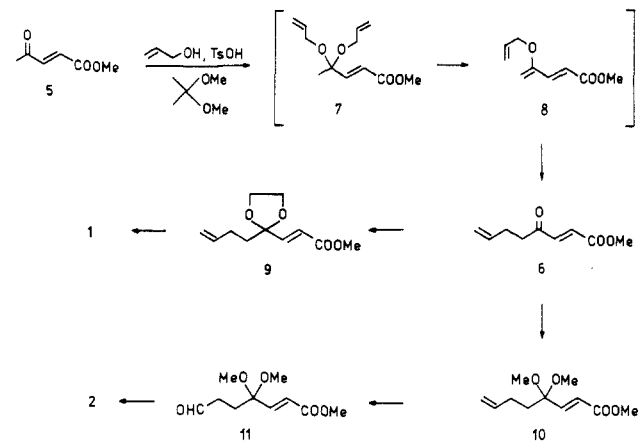
The key step consists of a Claisen rearrangement with in situ formation of an enol allyl ether from methyl 4-oxo-2-pentenoate (5), giving methyl 4-oxo-2,7-octadienoate (6) in good yield (Scheme I). The nature of the step 5 → 6, overall ketone α-allylation, is evident from the isolation of the intermediates 7 and 8 under less forcing conditions. After ketal formation, the protected pyrenophorin monomer 1 is obtained directly from 9 in a one-pot reaction via mercuration–reduction under basic conditions which also serve to hydrolyze the ester function. The corresponding tetrahydropyranacetic acid derivative, formed by Michael cyclization of 1, was also isolated here as a minor byproduct. Previously, three routes have been described for the synthesis of 1, each in eight steps in 15–20% overall yield, and thence pyrenophorin. The present route comprises four steps in 20% overall yield.

For the synthesis of the protected vermiculine monomer, the carbonyl-protected derivative 10 is selectively ozonized at the terminal double bond to give the aldehyde 11. The reaction of 11 with diisobutenylcadmium then completes the synthesis of 2. The corresponding hydroxy acid has been previously taken to vermiculine and was obtained[3b] via a six-step sequence from dimethyl 2-oxoglutarate. The present route comprises five steps in 16% overall yield.

Scheme I



Experimental Section

NMR spectra were recorded on a JEOL JNM-FX 60 at 59.75 MHz for ^1H and 15.00 MHz for ^{13}C. $CDCl_3$ was used as solvent with Me_4Si as internal standard in all NMR samples. IR spectra were obtained on a Perkin-Elmer 700 spectrometer. Mass spectra were recorded on a Perkin-Elmer 270 mass spectrometer. Microanalyses were performed by Novo Microanalytical Laboratory, Bagsvaerd, Denmark.

Methyl 4-Oxo-2-pentenoate (5). This compound was obtained as described for the corresponding ethyl ester:[4] mp 59 °C (EtOH); ^1H NMR δ 2.38 (s, 3 H), 3.83 (s, 3 H), 6.85 (AB q, 2 H, J = 16 Hz). Anal. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29. Found: C, 56.31; H, 6.31.

Methyl 4-Oxo-2,7-octadienoate (6). A mixture of 5 (25 g, 0.195 mmol), $Me_2C(OMe)_2$ (385 g, 3.7 mol), allyl alcohol (581 g, 10.0 mol), and TsOH (5 g, 0.026 mol) in toluene–xylene (1000 + 700 mL) was distilled during 8 h until the temperature reached 115 °C. The residue was washed with saturated $NaHCO_3$ solution and distilled [bp 87–95 °C (1.0 torr)] to give 6 (29.2 g, 89%) (for spectra, see ref 5).

Methyl 4,4-(Ethylenedioxy)-2,7-octadienoate (9). A mixture of 6 (6.60 g, 39 mmol), $(CH_2OH)_2$ (3.72 g, 60 mmol), and $(EtO)_3CH$ (5.93 g, 40 mmol) was refluxed for 18 h in benzene (150 mL) in the presence of $BF_3{\cdot}Et_2O$ (5 drops). It was then washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated. The residue was distilled to give 9 (7.27 g, 88%): bp 75–80 °C (0.1 torr); ^1H NMR δ 1.65–2.50 (m, 4 H), 3.75 (s, 3 H), 3.95 (s, 4 H), 4.80–5.25 (m, 2 H), 5.50–5.85 (m, 1 H), 6.45 (AB q, 2 H, J = 16 Hz); ^{13}C NMR δ 27.3, 33.9, 48.5, 51.3, 100.7, 114.4, 124.0, 137.4, 146.6, 166.2. Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.04; H, 7.52.

4,4-(Ethylenedioxy)-7-hydroxy-2-octenoic Acid (1) and 3,3-(Ethylenedioxy)-6-methyltetrahydropyran-2-acetic Acid. The ester 9 (420 mg, 2 mmol) in THF (5 mL) was rapidly added to a well-stirred solution of $Hg(OAc)_2$ (640 mg, 2 mmol) in H_2O/THF (5 + 5 mL). After 1 min, 5 mL of aqueous 3 N NaOH and 5 mL of a 0.5 M solution of $NaBH_4$ in 3 N NaOH were added. After 1 h, the mixture was filtered, and the cooled (0 °C) filtrate acidified to pH 3 with dilute H_2SO_4 and immediately extracted with ether (3 × 30 mL). The combined extracts were dried over $MgSO_4$ and evaporated. Preparative TLC (silica gel, $CHCl_3$/AcOH, 95:5) gave, as the less polar fraction, 208 mg (48%) of 1 as a viscous oil: ^1H NMR δ 1.20 (d, 3 H, J = 6 Hz), 1.30–2.15 (m, 4 H), 3.80 (m, 1 H), 3.96 (s, 4 H), 6.47 (AB q, 2 H, J = 16 Hz), 8.72 (br s, 2 H); ^{13}C NMR δ 23.1, 32.1, 33.6, 64.8, 67.8, 108.0, 121.4, 147.7, 169.9. Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.42; H, 7.46. The more polar fraction gave 26 mg (6%) of the tetrahydropyran-2-acetic acid (Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.27; H, 7.41) which was treated with ethereal CH_2N_2 to afford the methyl ester: IR (KBr) 1740 cm^{-1}; ^1H NMR δ 1.18 (d, 3 H, J = 6 Hz), 1.40–1.85 (m, 4 H), 2.53 (d, 2 H, J = 6 Hz), 3.20–3.81 (m, 2 H), 3.70 (s, 3 H), 4.00 (s, 4 H); ^{13}C NMR δ 21.1, 31.8, 32.9, 34.2, 51.4, 64.7, 65.2, 73.8, 77.9, 105.3, 171.9; mass spectrum, m/z (relative intensity) 230 (3, M^+·).

Methyl 4,4-Dimethoxy-2,7-octadienoate (10). The ester 6 (1.68 g, 10 mmol) was stirred for 4 h at −50 °C in 8 mL of MeOH in the presence of 5.2 g (50 mmol) of $Me_2C(OMe)_2$ and anhydrous TsOH (0.172 g, 1 mmol). After 12 h at room temperature, ether (50 mL) was added, and the solution was washed with dilute $NaHCO_3$ solution and dried over $MgSO_4$. Dry column chromatography (silica gel, hexane/$CHCl_3$, 1:1) gave 1.44 g (67%) of 10; ^1H NMR δ 1.87 (br s, 4 H), 3.21 (s, 6 H), 3.79 (s, 3 H), 4.76–5.17 (m, 2 H), 5.48–5.73 (m, 1 H), 6.46 (AB q, 2 H, J = 17 Hz). Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.84; H, 8.33. The above reaction at room temperature favors acid-catalyzed Michael addition of MeOH, presumably at C-2. The resulting product may however be recycled ($BF_3{\cdot}Et_2O$ in xylene at reflux) back to 6.

Methyl 4,4-Dimethoxy-7-oxo-2-heptenoate (11). The preceding ester 10 (8.63 g, 40 mmol) and pyridine (3.164 g, 40 mmol) in CH_2Cl_2/MeOH (50 + 50 mL) were treated with O_3/air at −90 °C, the reaction being monitored by TLC. After almost all starting material had been consumed, Me_2S (5.10 g, 82 mmol) was added and the reaction mixture was slowly allowed to warm up. CH_2Cl_2 (200 mL) was then added and the solution washed with water (5 × 50 mL). After the solution was dried over $MgSO_4$, dry column chromatography (silica gel, $CHCl_3$/EtOAc, 9:1) afforded 11 (5.127 g, 59%); ^1H NMR δ 1.83–2.43 (m, 4 H), 3.20 (s, 6 H), 3.78 (s, 3 H), 6.43 (AB q, 2 H, J = 16 Hz), 9.76 (s, 1 H).

Methyl 4,4-Dimethoxy-7-hydroxy-9-methyl-2,9-decadienoate (2). Anhydrous $CdBr_2$ (6.81 g, 25 mmol) was added with stirring to a Grignard reagent made from Mg (13.65 g, 150 mmol) and 3-chloro-2-methyl-1-propene (4.53 g, 50 mmol) in dry Et_2O/THF (55 + 10 mL). The preceding ester 11 (1.081 g, 5 mmol) in dry Et_2O (5 mL) was then added at 0 °C. After 30 min, 20% aqueous NH_4Cl solution was added, and the mixture was extracted with Et_2O (3 × 50 mL). Preparative TLC (silica gel, $CHCl_3$/EtOAc, 9:1) gave 2 as a viscous oil (1.064 g, 78%): ^1H NMR δ 1.10 (s, 1 H), 1.34–2.20 (m, 6 H), 1.74 (br s, 3 H), 3.23 (s, 6 H), 3.53 (s, 1 H), 3.80 (s, 3 H), 4.65–5.12 (m, 2 H), 6.59 (AB q, 2 H, J = 16 Hz); ^{13}C NMR δ 22.2, 30.7, 31.2, 46.0, 48.5, 48.7, 51.4, 68.2, 101.0, 113.3, 124.0, 142.3, 146.7, 166.3. Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.42; H, 8.67.

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Registry No. (±)-1, 70942-97-1; (±)-2, 77611-14-4; (±)-3, 38634-44-5; (±)-4, 55781-72-1; 5, 4188-88-9; 6, 77611-15-5; 9, 77611-16-6; 10, 77611-17-7; 11, 77611-18-8; 3,3-(ethylenedioxy)-6-methyltetrahydropyran-2-acetic acid, 77629-02-8; 3-chloro-2-methyl-1-propene, 563-47-3.

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

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

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

$$3 + 1^{+}\cdot \rightleftarrows 3^{+}\cdot + 1 \quad (3)$$

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

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