

thesis: it illustrates the applicability of this straightforward route to the synthesis of fluorine-substituted polycyclic aromatic hydrocarbons. The versatility of the reaction is manifested by the feasibility of directing the reaction to conventional as well as unconventional sites of substitution, thus leading to novel fluoropolycyclic aromatic compounds.

Experimental Section

Melting points were taken on a Tottoli Buchi capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in KBr disks. Ultraviolet spectra were recorded on a Unicam Model SP800A spectrophotometer. The ^1H and ^{19}F NMR spectra were taken on a Varian HA-100 spectrometer at 100 and 94.1 MHz, respectively. ^1H chemical shifts are reported in parts per million downfield from Me_4Si (internal standard). ^{19}F chemical shifts are reported in parts per million downfield from C_6F_6 (internal standard). Mass spectra were measured on a Varian MAT-311 instrument operating at 70 eV, employing the direct insertion technique. The mass spectra of the compounds reported below contained the appropriate signals representing the molecular ions. Analytical TLC separations were carried out at 24° on precoated plastic sheets (layer thickness 0.2 mm), Polygram Sil N-HR/UV₂₅₄ and Polygram Alox N/UV₂₅₄ (Machery-Nagel and Co.). Materials were detected with uv light. Pyrene (1) was obtained from Fluka AG (Buchs, Switzerland) and was further purified by recrystallization [dichloromethane-petroleum ether (bp 40–60°)]. Xenon difluoride was prepared by thermal means from xenon and fluorine, according to the procedure of Schreiner et al.²² No special precautions were taken to purify the XeF_2 completely from HF.

Fluorination of Pyrene with Xenon Difluoride. Method A. Reaction in a Vacuum Line System. Xenon difluoride (0.90 g, 5.3 mmol) was transferred to a Kel-F tube. A solution of pyrene (1, 2.18 g, 10.7 mmol) in 10 ml of dry dichloromethane was introduced into a second Kel-F tube. Both tubes were connected via a flexible Kel-F line. The tube containing the organic solution was degassed by the freeze-thaw technique until a pressure change after freezing to -125° was $<10^{-4}$ mm. The tube containing the XeF_2 was cooled to -78° and evacuated to 10^{-4} mm. The organic solution was then poured under vacuum into the Kel-F tube containing the XeF_2 at -195° . Upon warming to -125° no reaction was observed. Upon warming to -78° , the colorless reaction mixture turned dark blue, and xenon evolution was indicated. The reaction tube was occasionally shaken until the evolution of xenon ceased. After 8 hr the reaction appeared to be completed. The mixture was diluted with dichloromethane (50 ml), washed successively with aqueous sodium bicarbonate (5%, 20 ml) and water, and dried (Na_2SO_4), and the solvent was evaporated to dryness under vacuum. The remaining oily crude product was chromatographed on a column of silica gel, petroleum ether (bp 40–60°) serving as an eluent. The following compounds were isolated.

1-Fluoropyrene (2): mp $135\text{--}136^\circ$ (from petroleum ether) (lit.¹⁶ mp $136\text{--}137^\circ$); yield 16%; R_f (silica gel, petroleum ether) 0.72. Anal. Calcd. for $\text{C}_{16}\text{H}_9\text{F}$: C, 87.27; H, 4.09; F, 8.63. Found: C, 86.81; H, 4.32; F, 8.55. Uv max (cyclohexane) 233 nm ($\log \epsilon$ 4.58), 242 (4.78), 264 (4.34), 274 (4.53), 297 s (3.48), 308 (3.87), 322 (4.19), 338 (4.34), 358 (3.11), 361 s (3.06) 369 (2.72), 378 (3.01), and 382 (3.00); ir max (KBr) 2930, 1602, 1498, 1460, 1438, 1250, 831, and 707 cm^{-1} ; ^{19}F NMR δ (CDCl_3)²³ 43.2 ppm (q, $J_1 = 10.0$, $J_2 = 5.4$ Hz).

2-Fluoropyrene (3): mp $147\text{--}148^\circ$ (from ethanol) (lit.¹⁷ mp $151\text{--}152^\circ$); yield 11%; R_f (silica gel, petroleum ether) 0.76. Anal. Found: C, 87.00; H, 4.05; F, 8.55. Uv max (cyclohexane) 233 nm ($\log \epsilon$ 4.62), 242 (4.86), 252 s (4.38), 338 (4.45), 358 (3.21), 370 (2.78), 378 (3.22), and 382 (3.02); ir max (KBr) 2927, 1598, 1490, 1452, 1435, 1248, 830, and 703 cm^{-1} ; ^{19}F NMR δ (CDCl_3) 38.8 ppm (t, $J = 9.2$ Hz).

4-Fluorination Product: mp $142\text{--}144^\circ$ (from petroleum ether); yield 0.7%; R_f (silica gel, petroleum ether) 0.78; uv max (cyclohexane) 234 nm ($\log \epsilon$ 4.03), 243 (4.23), 262 (3.75), 273 (3.97), 296 (3.08), 308 (3.40), 322 (3.76), 337 (3.96), 343 s (2.42), 361 s (2.63), 366 (2.79), 380 (2.70), and 386 (2.92); ir max (KBr) 2920, 1600, 1500, 1452, 1438, 1283, 1250, 1070, 832, and 702 cm^{-1} ; ^{19}F NMR δ (CDCl_3) 42.1 ppm (d, $J = 10.8$ Hz).

Pyrene-Fluoropyrene Dimers. These were eluted from the column with petroleum ether-ether mixtures, mp ca. 268° , yield ca. 25%.

Fluorination of Pyrene with Xenon Difluoride. Method B.

Reaction in an Open System. A solution of pyrene (1, 2.446 g, 14.1 mmol) in dry dichloromethane (16 ml) was added, at -75°C under anhydrous conditions, to xenon difluoride (2.38 g, 14.1 mmol) in a Kel-F tube. The reaction mixture, which immediately turned dark blue, was occasionally shaken, and xenon evolution was observed. After 6 hr, the reaction seemed to be completed. The reaction complex was diluted with dichloromethane (50 ml) and decomposed with aqueous sodium bicarbonate (5%). The organic layer was washed with water and dried (Na_2SO_4) and the solvent was removed under vacuum. The remaining oily crude product was chromatographed as described above (method A). Yields: 2, 22%; 3, 14%; 4-fluorination product, 0.9%; "dimers", ca. 25%.

Registry No.—1, 129-00-0; 2, 1691-65-2; 3, 1714-25-6; 4, 56744-05-9; xenon difluoride, 13709-36-9.

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Fluorination with Xenon Difluoride. The Reactivity of Phenanthrene

Marko Zupan^x and Alfred Pollak

*J. Stefan Institute and Department of Chemistry,
University of Ljubljana, 61000 Ljubljana, Yugoslavia*

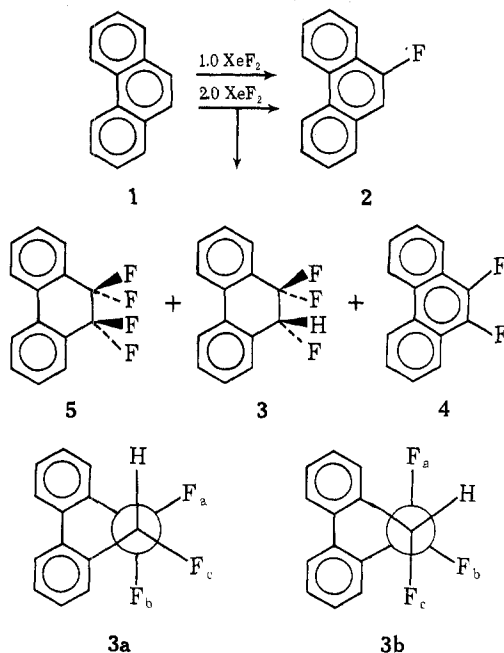
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Recently, we have found that xenon difluoride readily adds fluorine to 1,1-diphenylethylenes¹ and stilbene² in hydrogen fluoride catalyzed reactions to form the corresponding vicinal difluorides in high yield. Although the fluorination of benzene^{3,4} and its substituted derivatives^{5,6} has been investigated, there has been, up to now, no report of a similar fluorination of a polynuclear aromatic system with this reagent. Phenanthrene is well known to undergo addition across the 9,10 positions accompanying substitution in chlorination⁷ and bromination.⁸ It seemed to us, therefore, of interest to explore whether the addition of fluorine will compete with the substitution in the fluorination of this ar-

omatic system with xenon difluoride. We now report the results of such a study.

A 3-hr reaction of phenanthrene (1) with 1.0 molar equiv of XeF₂ and anhydrous HF as catalyst in methylene chloride at 25°C gave a reaction mixture from which two pure products could be separated by preparative GLC. One of them, obtained in 30% yield, was identified with unreacted 1 and the second one with 9-fluorophenanthrene⁹ in 60% yield.

A 24-hr reaction of 1 with 2.0 molar equiv of XeF₂ gave an oily reaction mixture. Its mass spectrum showed prominent peaks at *m/e* 196, 214, and 234 and a low intensity at *m/e* 252 indicating the presence of mono-, di-, tri-, and tetrafluoro compounds. Preparative GLC afforded four pure products. One of them was identified with 2 (in 46% yield) and the second one with 9,9,10,10-tetrafluoro-9,10-dihydrophenanthrene¹⁰ (5). The third, oily product, obtainable in only 3% yield, was assigned the structure of 9,10-difluorophenanthrene (4) on the basis of its spectral data. The structure assignment of the fourth reaction product, i.e., 9,10,10-trifluoro-9,10-dihydrophenanthrene (3), a colorless oil (20% yield), was made on the basis of its ¹H and ¹⁹F NMR and mass spectrum. As presented in Table I, the 9 proton is coupled to one geminal and two nonequivalent vicinal fluorine nuclei. Following the Karplus equation¹¹ for ³*J*(H-F_{vic}) dependence of dihedral angle, *J*_{HF_b} ≠ *J*_{HF_a} should be observed for the conformation 3a and *J*_{HF_b} = *J*_{HF_a} for 3b. The obtained values, i.e., 12.0 and 5.2 Hz, therefore strongly support the preferred conformation 3a for 3 in CCl₄ solution at room temperature.



The mass spectra of 3 and 5 are also of interest, the loss of a CF₂X· (X = H, F) radical being most notable (25 and 17% relative abundance for X = H and X = F, respectively) at 70 eV. A rationalization, similar to that proposed for CH₃ radical loss from 9,10-dihydrophenanthrene¹² via a fluorene intermediate (6), might be proposed.

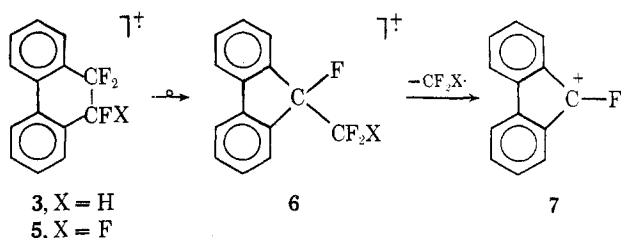


Table I
NMR Data for Compound 3^a

| | |
|-----------------------------------|---|
| δH 5.32 (ddd, 1 H) | <i>J</i> _{F_aH} = 5.2 Hz |
| δF _a -121.5 (ddd, 1 F) | <i>J</i> _{F_bH} = 12.0 Hz |
| δF _b -132.0 (ddd, 1 F) | <i>J</i> _{F_aF_c} = <i>J</i> _{F_bF_c} = 16.5 Hz |
| δF _c -215.8 (dt, 1 F) | <i>J</i> _{F_cH} = 50 Hz <i>J</i> _{F_aF_b} = 276 Hz |

^a 94.1 MHz (CCl₄), Me₄Si or CCl₃F as internal standard.

The fluorination of 9-fluorophenanthrene (2) with 1.0 or 2.0 molar equiv of XeF₂ under the same reaction conditions gave 3 and 5 in higher yields, but the amount of 4 did not exceed 5%.

All our efforts to detect the primary addition product, i.e., 9,10-difluoro-9,10-dihydrophenanthrene, were unsuccessful. This addition product was either not formed at all or decomposed so rapidly during the reaction or isolation that it had escaped our method of analysis. However, the formation of 3 and 5 clearly showed that addition of fluorine took place with 2 and 4. The rather high reactivity of 4 for the further addition of fluorine is probably the reason for its low presence in the reaction mixtures. This phenomenon we also observed in the fluorination of phenylacetylenes with XeF₂,¹³ as we could not detect the primary adducts, i.e., the corresponding fluoro olefins thus appeared also to be more reactive toward the addition of fluorine than the parent phenylacetylenes. The possibility of the formation of 4 by the elimination of hydrogen fluoride from 3 was also ruled out, because under the reaction and the isolation conditions an authentic sample of trifluoro compound 3 did not give a detectable amount of 4.

Although the addition of fluorine to the phenanthrene system and the accompanying substitution were clearly evidenced, work is in progress to elucidate the mechanism of fluorination with xenon difluoride, which appears to be more complex in comparison to chlorination⁷ and bromination⁸ of this aromatic system.

Experimental Section

IR spectra were recorded by using a Perkin-Elmer 257 spectrometer, ¹H and ¹⁹F NMR spectra by a Jeol JNM-PS-100 from CCl₄ solution with Me₄Si as internal standard, and mass spectra were recorded on a CEC 21-110C spectrometer. Melting points were determined on a Kofler apparatus and are uncorrected. Gas-liquid partition chromatography was carried out on Varian Aerograph Model 1800.

Materials. The phenanthrene was obtained from commercial sources and purified to conform with published physical and spectral data. Xenon difluoride was prepared by the photosynthetic method¹⁴ and its purity was better than 99.5%. Methylene chloride was purified by literature methods¹⁵ and stored over molecular sieves. Hydrogen fluoride of Fluka Purum quality was used.

9-Fluorophenanthrene (2). To a solution of 1 (0.178 g, 1.0 mmol) in methylene chloride (6 ml), XeF₂ (0.169 g, 1 mmol) was added at 25°C and under stirring anhydrous HF (0.02 g, 1 mmol) was introduced into the reaction mixture. After a few seconds the colorless solution turned dark blue and xenon gas was slowly evolved. After 3 hr gas evolution had ceased and the reaction appeared to be complete. The reaction mixture was diluted with methylene chloride (15 ml), washed (10 ml of 5% aqueous NaHCO₃), and dried (Na₂SO₄) and solvent was evaporated in vacuo. The crude product was separated by preparative GLC (10% Carbowax 20M on Varaport 30, 210°C). Unreacted phenanthrene was isolated in 30% yield and 9-fluorophenanthrene (2) in 60% yield (0.1176 g); mp 51–52°C; ¹⁹F NMR (94.1 MHz, CCl₄) δ -138.0 (dd, *J*_{HF} = 12.8 and 2.3 Hz), high-resolution mass spectrum *m/e* 177.0693 (M - F)⁺ (calcd for C₁₄H₉, 177.0704).

9-Fluorophenanthrene (2), 9,9,10,10-Tetrafluoro-9,10-dihydrophenanthrene (5), 9,10-Difluoro-9,10-dihydrophenanthrene (4), and 9,10,10-Trifluoro-9,10-dihydrophenanthrene (3). To a solution of 1 (0.356 g, 2 mmol) in methylene chloride (15 ml), XeF₂ (0.677 g, 4 mmol) was added at 25°C and under stirring HF (0.080 g, 4 mmol) was introduced into the reaction mixture. After a few sec-

onds the colorless solution turned dark blue and xenon gas was slowly evolved. After 24 hr gas evolution had ceased and the reaction appeared to be complete. The reaction mixture was diluted with methylene chloride (30 ml), washed (20 ml of 5% aqueous NaHCO_3), and dried (Na_2SO_4) and solvent was evaporated in vacuo. The crude product was separated by preparative GLC (10% Carbowax 20M on Varaport 30, 210°C) and afforded as pure products the following.

9-Fluorophenanthrene (2) in 46% yield (0.180 g).

9,9,10,10-Tetrafluoro-9,10-dihydrophenanthrene (5) in 10% yield (0.050 g); mp 95–96°C; ^{19}F NMR (94.1 MHz, CCl_4) δ -134.2 (s); high-resolution mass spectrum m/e 176.0582 ($M - 4\text{F}$)⁺ (calcd for C_{14}H_8 , 176.0626).

9,10-Difluorophenanthrene (4), oily product in 3% yield (0.0128 g); ^{19}F NMR (CCl_4) δ -169.5 (s); mass spectrum m/e 214 (100%), 107 (9), 98 (11); high-resolution mass spectrum m/e 214.0574 (M^+) (calcd for $\text{C}_{14}\text{H}_8\text{F}_2$, 214.0603).

9,10,10-Trifluoro-9,10-dihydrophenanthrene (3), colorless oil in 20% yield (0.0936 g); mass spectrum m/e 234 (100%), 183 (25), 165 (6), 107 (6); high-resolution mass spectrum m/e 234.0631 (M^+) (calcd for $\text{C}_{14}\text{H}_9\text{F}_3$, 234.0669); NMR data are stated in Table I.

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Registry No.—1, 85-01-8; 2, 440-21-1; 3, 56830-33-2; 4, 56830-34-3; 5, 14205-64-2; XeF_2 , 13709-36-9.

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Direct Fluorination of Polycyclic Hydrocarbons with Xenon Difluoride

S. P. Anand,¹ Lloyd A. Quarterman,¹ Paul A. Christian,^{1,3} H. H. Hyman,^{1,4} and Robert Filler*²

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616, and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

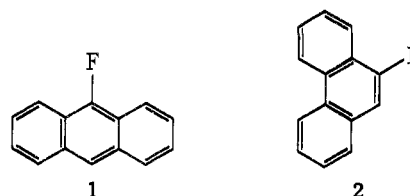
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In previous papers⁵ we described the usefulness of xenon difluoride for the introduction of fluorine into the aromatic nucleus. Recently, we reported⁶ that aryl oxygen compounds undergo rapid nuclear fluorination with XeF_2 , even in the absence of initiation by hydrogen fluoride.

We now report that this reaction has been extended to polynuclear aromatics, including naphthalene, anthracene, and phenanthrene. These compounds are converted with facility to monofluoro analogues which are not readily accessible by other means.⁷ Although initiation is not re-

quired, the addition of a trace of HF leads to an immediate and vigorous reaction.

The fluoro isomers obtained in these reactions were identified by comparison of their gas chromatograms and mass spectra (interfaced) with those of authentic samples. Thus, naphthalene, in methylene chloride solution, was converted to a mixture of 1-fluoronaphthalene (50% yield) and 2-fluoronaphthalene (11%). Similarly, anthracene in chloroform reacted with XeF_2 to give a mixture of three isomers. Column chromatography on neutral alumina of the reaction mixture derived from 10 mmol of anthracene gave 9-fluoroanthracene (1,⁸ 26%), 1-fluoroanthracene (45%),⁹ and 2-fluoroanthracene (9%).⁸ In analogous fashion and without addition of external HF, crystalline 9-fluorophenanthrene (2)¹⁰ was isolated in 40% yield. In addition, a



higher melting yellow substance, decomposing at 181–182°, was obtained. Although this material has not yet been characterized, its mass spectrum suggests a difluorophenanthrene.

In a separate experiment, a small amount of anhydrous HF was added to a mixture of phenanthrene and XeF_2 in methylene chloride. Although no products could be isolated, mass spectral analysis indicated the formation of difluoro, trifluoro, and tetrafluoro addition products. Similar results have been reported by Zupan and Pollak.¹¹ Although these reactions were carried out in a vacuum line system,^{5b} we have conducted several reactions with other substrates in an open system, with similar results. This adaptation markedly increases the attractiveness of this method.

As recently proposed,⁶ we believe that the reaction proceeds via cation radicals which are readily generated, owing to the facile one-electron transfer from the aromatic to the strongly oxidizing $[\text{XeF}]^+$ species.

These observations, together with the recent findings on the fluorination of pyrene with XeF_2 ,¹² further extend the scope and potential of this unusual one-step fluorination of aromatic molecules.

Experimental Section

Materials. Xenon difluoride was prepared photosynthetically according to a procedure described previously.⁶ Purified solvents and reagents of AR grades were used and handled under a dry nitrogen atmosphere. Melting points were determined on a Fisher-Johns block and are uncorrected. All gas chromatographic data were recorded on a Perkin-Elmer Model 900 instrument equipped with a flame ionization detector. Mass spectra were recorded on a Bendix time-of-flight instrument and some GC-MS data were obtained on a Finnegan Model 3000 instrument. All reactions were carried out in Kel-F tubes of about 30 ml capacity fitted with 0.25-in. brass valves⁵ and under reduced pressure (10^{-5} – 10^{-6} Torr). A small portion of the reaction mixture, when removed for GC or MS analysis, was always treated with sodium fluoride pellets to remove hydrogen fluoride produced during the course of the reaction. The remainder of the reaction mixture was dried under reduced pressure at room temperature to remove the solvents as well as HF.

Naphthalene and XeF_2 . A solution of 1.47 g (11.5 mmol) of naphthalene in 15 ml of methylene chloride was degassed up to 5×10^{-6} Torr and poured into 0.63 g (ca. 3.7 mmol) of XeF_2 contained in an evacuated Kel-F tube (10^{-6} Torr) at -196° . The reaction mixture was warmed gradually from -196° to -78° to 0° and finally to room temperature during a period of 2 hr. A deep green coloration and the evolution of gas bubbles were observed while