amounts of **4**. A VPC-purified sample (25 ft × 0.25 in. column containing 20% SF-1265 on Chromosorb W) gave pure **8**: $n^{27.0}D$ 1.5326; ir (neat film) 1708 w, 1290 s, 1070 s, 820 m, and 708 cm^{-1} m; MS *m/e* 282, 280 (M^+), 263, 261, 232, 230, 201 (base peak), 155, 153, 127, and 74. The ^{19}F NMR spectrum gave a singlet at 100.5 ppm upfield from F-11 (Cl_3CF).

Acknowledgments. We wish to thank the Robert A. Welch Foundation (Grant AF-585) for their generous support of this work. The invaluable assistance of Dr. Ben Shoulders and Mr. F. C. Maseles in obtaining the NMR and mass spectra is also gratefully acknowledged.

Registry No.—**1**, 6262-51-7; **2**, 6262-42-6; **3**, 6262-45-9; **4**, 56830-73-0; **5**, 56830-74-1; **6**, 6262-43-7; **7**, 6262-46-0; **8**, 56840-75-2; sodium trichloroacetate, 2923-18-4; trichloroethylene, 79-01-6; antimony trifluoride, 7783-56-4; potassium iodide, 7681-11-0.

References and Notes

(1) R. L. Soulen, B. T. Nakata, and J. D. Park, *J. Fluorine Chem.*, **1**, 235 (1971–1972).
(2) R. Sullivan, J. R. Lacher, and J. D. Park, *J. Org. Chem.*, **29**, 3664 (1964).
(3) J. D. Park, C. D. Bertino, and B. T. Nakata, *J. Org. Chem.*, **34**, 1490 (1969).
(4) G. Camaggi, *J. Chem. Soc. C*, 2382 (1971).
(5) R. L. Soulen, S. K. Choi, and J. D. Park, *J. Fluorine Chem.*, **3**, 141 (1973–1974).
(6) R. D. Chambers, "Fluorine in Organic Chemistry", Wiley-Interscience, New York, N.Y., 1973, p 344 ff.
(7) J. D. Park and S. K. Choi, *Daehan Hwahak Hwoejee*, **17**, 286 (1973); *Chem. Abstr.*, **79**, 105369m (1973).
(8) H. M. Cohen and A. H. Keough, *J. Org. Chem.*, **31**, 3428 (1966).
(9) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2478, 2481 (1966).
(10) D. C. F. Law, S. W. Tobey, and R. West, *J. Org. Chem.*, **38**, 768 (1973).
(11) P. B. Sargent and C. G. Krespan, *J. Am. Chem. Soc.*, **91**, 415 (1969).
(12) J. A. Riddick and W. B. Bunger, "Organic Solvents, Techniques of Chemistry", Vol. 2, 3rd ed, Wiley-Interscience, New York, N.Y., 1970.

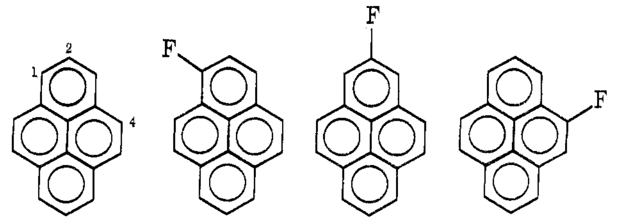
Reaction of Xenon Difluoride with Polycyclic Aromatic Hydrocarbons. Fluorination of Pyrene

Ernst David Bergmann,[1,2a] Henry Selig,[2b] Chun-Hsu Lin,[2a] Mordecai Rabinovitz,[2a] and Israel Agranat*[2a]

Department of Organic Chemistry and Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

Received May 12, 1975

Fluorine-substituted condensed polycyclic aromatic hydrocarbons and heterocyclics are of interest in experimental carcinogenesis.[3-5] Heretofore, their syntheses were based mostly on the following two general methods. (a) A "tailor-made" sequence analogous to the one applied in a well-established synthesis of the corresponding polycyclic hydrocarbon, but with a fluorine-substituted starting material (e.g., 3-fluorophthalic anhydride,[6] 4-fluoro-1-bromonaphthalene[7]). (b) A direct electrophilic substitution of the polycyclic aromatic hydrocarbon followed by appropriate transformations of the substituent to fluorine[8] (e.g., ArH → $ArNO_2$ → $ArNH_2$ → $ArN_2^+BF_4^-$ → ArF and ArH → $ArSO_3H$ → ArOH → ArOCOF → ArF). In the latter method, the fluorine is usually introduced at the most reactive sites of the hydrocarbon. Neither method is very satisfactory. Direct methods for the introduction of a fluorine atom into polycyclic aromatics are still in their infancy. Recently, xenon difluoride has been shown to act as an efficient and selective fluorinating agent for simple aromatic compounds, both in solution and in the vapor phase.[9-14] The reaction is catalyzed by HF and does not proceed without it.[11,15] We report the application of this direct fluorination route in the aromatic polycyclic series. Pyrene (**1**) was se-



1 **2** **3** **4**

lected as a model substrate for examining the mode of the reaction of xenon difluoride with polycyclic aromatic hydrocarbons. The convenience of pyrene stemmed from its high symmetry (point group D_{2h}), its tetracyclic structure, and the presence of three characteristic substitution sites (1, 2, and 4) which lend themselves readily to identification by ^{19}F NMR spectra (vide infra).

The reaction of xenon difluoride and pyrene was carried out in a vacuum line system as well as in an open system. Both experiments were performed under anhydrous conditions. The products were separated from the crude reaction mixture by column chromatography on silica gel.

The major monomeric products of the reaction (apart from the starting material **1**), were 1-fluoropyrene (**2**, 16–22% yield) and 2-fluoropyrene (**3**, 11–14% yield). Fluorination at the 4 position apparently also occurred, albeit in very low yields. The *patterns* of the ^{19}F NMR absorptions served as a probe for identifying the site of the fluorination. The 1 isomer (**2**) showed a quartet (at 43.2 ppm, J_1 = 10.0, J_2 = 5.4 Hz) while the 2 isomer (**3**) showed a triplet (at 38.9 ppm, J = 9.2 Hz). Fluorination at the 4 position was indicated by a ^{19}F NMR doublet (at 42.1 ppm, J = 10.8 Hz). However, this product could not be purified and analyzed adequately and its structure [perhaps 4-fluoropyrene (**4**)] has not been established. The melting point of **2** was practically identical with that reported in the literature.[16] The melting point of **3** (147–148°) was very similar to that reported by Jensen and Berg (151–152°).[17] The structures of **2** and **3** were supported also by the elemental analyses and the appropriate molecular ions in the mass spectra. The 1 isomer (**2**) has previously been prepared by the conventional Balz–Schieman method.[16] Very low yields of **2** (as a picrate) were obtained also by a direct fluorination of pyrene with *p*-tolyl iododifluoride.[16] The 2 isomer (**3**) has previously been prepared by the use of cine substitution via a 1,2-dehydropyrene intermediate: 1-bromopyrene was converted to a mixture of 1- and 2-aminopyrene, the amines were separated, and 2-aminopyrene was transformed by the Balz–Schieman method to **3**.[17,18] The fluorination of pyrene with xenon difluoride yielded also appreciable amounts (ca. 25%) of "dimeric" products [$(C_{16}H_9)_2$, $C_{16}H_8F)_2$, $C_{16}H_8F$–$C_{16}H_9$ (?), prominent mass spectral signals at *m/e* 438, 420, and 402] which were not further characterized. It should be noted that comparable results were obtained in an open system and in a vacuum line system. Furthermore, the XeF_2/pyrene ratio did not affect the yields of the various substitution products of the reaction.

The mass spectra of some fractions obtained from the chromatography, including the impure 4-fluorination product, indicated the formation of difluoropyrene isomers, but these could not be separated and characterized. It has recently been reported that xenon difluoride adds fluorine to the phenanthrene system to form vicinal difluorides.[19]

The relative yields of **2** and **3** are exceptional, in view of the overwhelming preference of position 1 as the initial site of electrophilic substitutions of pyrene.[18,20-21] It may reflect the lower degree of selectivity of the attacking species.

The direct fluorination of pyrene with xenon difluoride widens the scope and generality of this fluoroaromatic synthesis: 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/UV_{254} and Polygram Alox N/UV_{254} (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 135–136° (from petroleum ether) (lit.[16] mp 136–137°); yield 16%; R_f (silica gel, petroleum ether) 0.72. Anal. Calcd. for $C_{16}H_9F$: 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 ϵ 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 147–148° (from ethanol) (lit.[17] mp 151–152°); 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 ϵ 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 142–144° (from petroleum ether); yield 0.7%; R_f (silica gel, petroleum ether) 0.78; uv max (cyclohexane) 234 nm (log ϵ 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 raction 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.

References and Notes

(1) Deceased April 6, 1975, Jerusalem.
(2) (a) Department of Organic Chemistry; (b) Department of Inorganic and Analytical Chemistry.
(3) (a) E. C. Miller and J. A. Miller, *Cancer Res.*, **20**, 133 (1960); (b) J. A. Miller and E. C. Miller, *ibid.*, **23**, 229 (1963).
(4) M. S. Newman, J. Cecil, and W. Hung, *J. Med. Chem.*, **15**, 569 (1972).
(5) For structure–activity relationships of chemical carcinogens in the aromatic polycyclic series, see J. C. Acros and M. F. Argus, "Chemical Induction of Cancer", Vol. IIA, Academic Press, New York, N.Y., 1974, p 1.
(6) M. Bentov and E. D. Bergmann, *Bull. Soc. Chim. Fr.*, 963 (1963).
(7) E. D. Bergmann and J. Blum, *J. Org. Chem.*, **27**, 527 (1962).
(8) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969, p 417, and references cited therein.
(9) M. J. Shaw, H. H. Hyman, and R. Filler, *J. Am. Chem. Soc.*, **91**, 1563 (1969).
(10) M. J. Shaw, J. A. Weil, H. H. Hyman, and R. Filler, *J. Am. Chem. Soc.*, **92**, 5096 (1970).
(11) M. J. Shaw, H. H. Hyman, and R. Filler, *J. Am. Chem. Soc.*, **92**, 6498 (1970).
(12) M. J. Shaw, H. H. Hyman, and R. Filler, *J. Org. Chem.*, **36**, 2917 (1971).
(13) D. R. MacKenzie and J. Fajer, *J. Am. Chem. Soc.*, **92**, 4994 (1970).
(14) T. C. Shieh, E. D. Feit, C. L. Chernick, and N. C. Yang, *J. Org. Chem.*, **35**, 4020 (1970).
(15) An exception has recently been noted in aryl oxygen compounds which undergo rapid fluorination with xenon difluoride in the absence of hydrogen fluoride initiation. See S. P. Anand, L. A. Quarterman, H. H. Hyman, K. G. Migliorese, and R. Filler, *J. Org. Chem.*, **40**, 807 (1975).
(16) G. M. Badger and J. F. Stephens, *J. Chem. Soc.*, 3637 (1956).
(17) A. Jensen and A. Berg, *Acta Chem. Scand.*, **19**, 520 (1965).
(18) Cf. A. Streitwieser, Jr., R. G. Lawler, and D. Schwaab, *J. Org. Chem.*, **30**, 1470 (1965).
(19) Cf. M. Zupan and A. Pollak, *J. Org. Chem.*, **39**, 2646 (1974).
(20) L. F. Fieser and M. Fieser, "Topics in Organic Chemistry", Reinhold, New York, N.Y., 1963, p 34.
(21) E. Clar, "Polycyclic Hydrocarbons", Vol. 2, Academic Press, New York, N.Y., 1964, p 119.
(22) F. Schreiner, G. N. McDonald, and C. L. Chernick, *J. Phys. Chem.*, **72**, 1162 (1968).
(23) Cf. M. J. S. Dewar, R. C. Fahey, and P. J. Grisdale, *Tetrahedron Lett.*, 343 (1963).

Fluorination with Xenon Difluoride. The Reactivity of Phenanthrene

Marko Zupan* and Alfred Pollak

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

Received June 23, 1975

Recently, we have found that xenon difluoride readily adds fluorine to 1,1-diphenylethylenes[1] and stilbene[2] 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 chlorination[7] 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-