amounts of 4. A VPC-purified sample (25 ft x 0.25 in. column containing 20% SF-1265 on Chromosorb W) gave pure 8: \( n^2 D = 1.5392; \) ir (neat film) 1708 w, 1290 s, 820 m, and 708 cm\(^{-1}\) m; MS \( m/e \) 285, 280 (M\(^+\)), 265, 261, 232, 230, 201 (base peak), 156, 153, 157, and 74. The \(^{19}F\) NMR spectrum gave a singlet at 100.5 ppm upfield from F-11 (Cl\(_2\)CF).

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Registry No.—1, 6262-51-7; 2, 6262-42-6; 3, 6262-45-9; 4, 79-01-6; 5, 282-75-0; 6, 58350-74-1; 7, 6262-45-0; 8, 5640-75-2; sodium trifluoracetate, 292; 14, 250; trichloroethylene, 79-01-6; antimony trifluoride, 7783-56-4; potassium iodide, 7681-11-0.

References and Notes


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

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Fluorine-substituted condensed polycyclic aromatic hydrocarbons and heterocarbons 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-bromonaphthalene7). (b) A direct electrophilic substitution of the polycyclic aromatic hydrocarbon followed by appropriate transformations of the substituent to fluorine (e.g., ArH → ArNO₂ → ArNH₂ → ArNO₂F → ArF and ArH → ArSO₂H → ArOH → ArOCOF → ArF). In the latter methods, 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 selected 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 \( D_{4h} \)), 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, \( J_{12} = 5.4 \) 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\(^\circ\)C) was very similar to that reported by Jensen and Berg (151-152\(^\circ\)C).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.18 The 2 isomer (3) has previously been prepared by the use of cine substitution via a 1,2-dehydroxypropene 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 [(\( C_{16}H_{15}F \))\(_2\), \( C_{18}H_{15}F_2 \), \( C_{16}H_{16}F-C_{16}H_{16} \)], 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-fluoropyrene (4), showed a quartet (at 43.2 ppm, \( J_{12} = 5.4 \) Hz) and a triplet (at 38.9 ppm, \( J = 9.2 \) Hz). The fluorination of pyrene with xenon difluoride additive was found to be efficient and selective, and the products were readily characterized. Further investigations of the fluorination of pyrene with xenon difluoride are in progress.
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 fluropolycyclic 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 $^1$H and $^{19}$F NMR spectra were taken on a Varian HA-100 spectrometer operating at 100 and 94.1 MHz, respectively. $^1$H chemical shifts are reported in parts per million downfield from SiMe$_3$. $^{19}$F chemical shifts are reported in ppm (internal standard) downfield from CsF$_6$.

Reaction in an Open System. A solution of pyrene (1, 2,446 g, 14.1 mmol) in dry dichloromethane (16 ml) was added, at $-75^\circ$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$_2$SO$_4$) and the solvent was removed under vacuum. The remaining oily crude product was chromatographed as described above (method A). Yields: 2%; 2,5%; 3%; 4%; fluorination product, 0.9%; "dimers", ca. 25%.

Registry No.—1, 129-00-0; 2, 1691-65-2; 3, 1714-25-6; 4, 5674-05-9; xenon difluoride, 13708-36-9.

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Fluorination with Xenon Difluoride.

The Reactivity of Phenanthrene

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Recently, we have found that xenon difluoride readily adds fluorine to 1,1-diphenylethylene and stilbene in hydrofluoric acid catalyzed reactions to form the corresponding vicinal difluorides in high yield. Although the fluorination of benzene and its substituted derivatives 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 and bromination. 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-