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 $(M - 4F)^+$ (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 $C_{14}H_8F_2$, 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 $C_{14}H_9F_3$, 234.0669); NMR data are stated in Table I.

Acknowledgment. We thank Professor J. Slivnik for the XeF_2 and Professor J. Marsel for facilities. The financial assistance of the Boris Kidrič Foundation is acknowledged.

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.

References and Notes

(1) M. Zupan and A. Pollak, *J. Chem. Soc., Chem. Commun.*, 845 (1973).
(2) M. Zupan and A. Pollak, *Tetrahedron Lett.*, 1015 (1974).
(3) M. J. Shaw, H. H. Hyman, and R. Filler, *J. Am. Chem. Soc.*, **91**, 1563 (1969).
(4) D. R. Mackenzie and J. Fajer, *J. Am. Chem. Soc.*, **92**, 4994 (1970).
(5) M. J. Shaw, H. H. Hyman, and R. Filler, *J. Am. Chem. Soc.*, **92**, 6498 (1970).
(6) M. J. Shaw, H. H. Hyman, and R. Filler, *J. Org. Chem.*, **36**, 2917 (1971).
(7) P. B. D. de la Mare and R. Koenigsberger, *J. Chem. Soc.*, 5327 (1964).
(8) C. C. Price, *J. Am. Chem. Soc.*, **58**, 1834, 2101 (1936); L. Altschulter and E. Berliner, *Ibid.*, **88**, 5837 (1966); J. van der Linde and E. Havings, *Recl. Trav. Chim. Pays-Bas*, **84**, 1047 (1965).
(9) P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, 4486 (1955).
(10) L. N. Nikolenko and A. V. Potapova, *Zh. Obshch. Khim.*, **36**, 1815 (1966).
(11) A. M. Ihrig and S. L. Smith, *J. Am. Chem. Soc.*, **92**, 759 (1970).
(12) J. H. Bowie, P. F. Donaghue, J. H. Rodda, and B. K. Simons, *Tetrahedron*, **24**, 3965 (1968).
(13) M. Zupan and A. Pollak, *J. Org. Chem.*, **39**, 2646 (1974).
(14) S. M. Williamson, *Inorg. Synth.*, **11**, 147 (1968).
(15) J. H. Mathews, *J. Am. Chem. Soc.*, **48**, 562 (1926).

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]

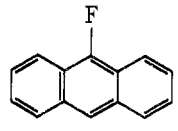
Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616, and Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Received July 8, 1975

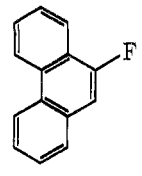
In previous papers[5] we described the usefulness of xenon difluoride for the introduction of fluorine into the aromatic nucleus. Recently, we reported[6] that aryl oxygen compounds undergo rapid nuclear fluorination with XeF_2, even in the absence of initiation by hydrogen fluoride.

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 required, 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



1



2

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 $[XeF]^+$ 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 valves[5] 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

the reaction mixture was allowed to warm to room temperature. The xenon which evolved was collected in a storage can and the resulting solution was distilled at 25° under vacuum into another Kel-F tube at −196°. Comparison of GC retention times of the distillate on a 12 ft × 0.125 in. column packed with 2.5% Apiezon L on Chromosorb W at 150° with those of authentic samples showed the formation of 1-fluoronaphthalene (50%) and 2-fluoronaphthalene (11%). Further analysis of the redistilled reaction mixture on a GC–MS instrument, using the same GC column, indicated that each peak consisted of a single component and had the correct parent ion mass and fragmentation pattern expected for the particular monofluoro substituted naphthalene. No attempt was made to separate the isomers physically from the reaction mixture. Some unreacted naphthalene was also found.

Reaction of Anthracene with XeF_2. A degassed solution of 1.78 g (10 mmol) of anthracene in 15 ml of chloroform up to 10^{-5} Torr was introduced into an evacuated (5×10^{-6} Torr) Kel-F tube containing 0.67 g (ca. 4.0 mmol) of XeF_2 at −196°. After the gradual increase of the temperature to −12°, a light yellow solution formed which intensified into a deep green by increasing the temperature to 12° during a period of 4 hr. The reaction products were filtered through a glass wool plug into another Kel-F tube under vacuum. The course of reaction as followed by GC, using an 11 ft × 0.125 in. column packed with 2.5% Carbowax 20 mesh on Chromosorb G at 225° indicated no unreacted anthracene and comparison of the data with those of authentic samples showed the formation of 1-fluoroanthracene, 2-fluoroanthracene, and 9-fluoroanthracene in the relative ratio of 5:1:3, based on their relative retention times. The mass spectra (interfaced with GC) were used to identify the three components and analysis of the fragmentation patterns and maximum mass peaks of each component allowed assignment of three of the peaks to monofluoroanthracenes. The distillate was concentrated almost to dryness under reduced pressure and chromatographed on an 18 × 1.5 in. column packed with neutral alumina. By eluting the column with *n*-hexane, 9-fluoroanthracene, mp 102° (lit.[8] 103°), was obtained as light lemon-colored crystals, which sublimed under vacuum at 78° (yield 26%), followed by pale yellow crystals of 1-fluoroanthracene, mp 108° (lit.[9] 108°), which sublimed in vacuo at 80° (yield 45%). Further elution with *n*-hexane–chloroform (3:1) gave yellow, crystalline 2-fluoroanthracene, mp 212° (lit.[8] 212°), which was crystallized from ethanol to give sublimable yellow crystals (yield 9%). An unidentifiable dark brown solid was obtained by eluting the column with *n*-hexane–$CHCl_3$ (1:1), while another deep pink material, which did not dissolve even in tetrahydrofuran and methanol, remained behind.

Reaction of Phenanthrene with XeF_2. XeF_2 (0.43 g) contained in a Kel-F tube was allowed to react with a degassed solution of 1.1 g (ca. 6 mmol) of phenanthrene in 10 ml of methylene chloride at 10^{-5} Torr at −196°. The solution was gradually warmed from −196° to room temperature during a period of 2 hr by means of a series of baths to give a brown-green reaction mixture which was further warmed in a water bath at 60° to ensure complete reaction. The course of reaction, followed by GC, using the same column described for the anthracene reaction mixture, indicated the presence of one fluoro derivative in addition to some unreacted phenanthrene.

The reaction mixture was freed from the solvent as well as HF under reduced pressure and the deep green solid was chromatographed on an 18 × 1.5 in. column packed with Florisil. Elution with *n*-hexane gave a 40% yield of a colorless, crystalline compound, 9-fluorophenanthrene, which was crystallized from petroleum ether (bp 30–60°) to give colorless needles, mp 50° (lit.[10] 51–52°). The rest of the material, on further elution with *n*-hexane–CH_2Cl_2 (10:3), gave a bright yellow substance which was crystallized from petroleum ether–$CHCl_3$ (1:1) to give a yellow compound which decomposed at 181–182° to a brown mass and presumably is a difluorophenanthrene as inferred from the highest mass fragment obtained in its MS, *m/e* 214 (100%), $C_{14}H_8F_2$.

In another experiment, 0.51 g (2.8 mmol) of phenanthrene and 8 ml of CH_2Cl_2 were allowed to react with 0.5 g (ca. 3 mmol) of XeF_2 under similar conditions in the presence of 0.05 mmol of anhydrous HF. On warming the reaction mixture to 0°, an intense green color developed, with brisk evolution of xenon gas. At room temperature, the mixture turned to dark magenta after 15 min. The course of reaction as followed by GC indicated the absence of any phenanthrene and no formation of any monofluoro species as found in the previous experiment. The MS interfaced with GC indicated the formation of difluoro, trifluoro, and tetrafluoro addition products of phenanthrene. However, no polyfluoro compounds could be isolated either by column chromatography or crystallization. A separate analysis of the fragmentation patterns and maximum mass peaks of each component permitted identification of the di-, tri-, and tetrafluoro compounds.

Acknowledgments. We wish to thank Drs. M. Studier and L. Kaplan for assistance with the mass spectra and gas chromatography, respectively. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support (to R.F.) of this research.

Registry No.—**1**, 529-85-1; **2**, 440-21-1; naphthalene, 91-20-3; XeF_2, 13709-36-9; 1-fluoronaphthalene, 321-38-0; 2-fluoronaphthalene, 323-09-1; anthracene, 120-12-7; 1-fluoroanthracene, 7651-80-1; 2-fluoroanthracene, 21454-60-4; phenanthrene, 85-01-8.

References and Notes

(1) Argonne National Laboratory.
(2) Illinois Institute of Technology.
(3) 1972 Honors Research Program Participant.
(4) Deceased, July 20, 1973.
(5) (a) M. J. Shaw, H. H. Hyman, and R. Filler, *J. Am. Chem. Soc.*, **92**, 6498 (1970); (b) M. J. Shaw, H. H. Hyman, and R. Filler, *J. Org. Chem.*, **36**, 2917 (1971).
(6) S. P. Anand, L. A. Quarterman, H. H. Hyman, K. G. Migliorese, and R. Filler, *J. Org. Chem.*, **40**, 807 (1975).
(7) An exception is the use of CF_3OF to prepare fluoronaphthalenes: T. B. Patrick and E. C. Hayward, *J. Org. Chem.*, **39**, 2120 (1974).
(8) G. L. Anderson and L. M. Stock, *J. Org. Chem.*, **36**, 1140 (1971).
(9) M. J. S. Dewar and J. Michl, *Tetrahedron*, **26**, 375 (1970).
(10) M. A. Goldberg, E. P. Ordas, and G. Carsch, *J. Am. Chem. Soc.*, **69**, 260 (1947).
(11) M. Zupan and A. Pollak, *J. Org. Chem.*, **39**, 2646 (1974).
(12) E. D. Bergmann, H. Selig, C.-H. Lin, M. Rabinovitz, and I. Agranat, *J. Org. Chem.*, **40**, 3793 (1975).

Reduction of Bromohydrins to Olefins with Low Valent Titanium

John E. Mc Murry* and Tova Hoz

Thimann Laboratories, University of California, Santa Cruz, California 95064

Received July 10, 1975

Although the reduction of bromohydrins to olefins is of some importance in synthesis, few direct methods have been devised to effect the reaction. To our knowledge, only the well-known zinc–acetic acid method has been used to any extent,[1] although chromous ion has been shown to be effective[2] and has been studied in some detail. Low valent tungsten halides also appear to work, but details are not available.[3]

We have been involved recently in a study of low valent titanium reagents for use as reducing agents in organic synthesis,[4] and among the substrates we have examined have been some representative bromohydrins. We have found that a reagent prepared by mixing 1 molar equiv of $LiAlH_4$ with 0.25 molar equiv of $TiCl_3$ in tetrahydrofuran is extremely effective in reducing bromohydrins to olefins. Some of our results are given in Table I.

From a synthetic point of view, several comments should be made. The first is that all substrates studied reduced in high yields indicating the generality of the reaction. Second is the fact that the reaction conditions are nonacidic, making the method compatible with the presence of acid-sensitive functional groups and quite different from the other methods. Finally, we note from the reductions carried out on *erythro*- and *threo*-5-decene bromohydrins, that these reactions proceed with little stereoselectivity. In this respect, the results are similar to those obtained both with zinc[5] and with chromous ion.[2]