CHEMISTRY LETTERS, pp. 1271-1272, 1975. Published by the Chemical Society of Japan

FACILE FLUORINATION OF PHENANTHRENE BY XENON DIFLUORIDE: VERSATILE SUBSTITUTION AND ADDITION, WITHOUT HYDROGEN FLUORIDE INITIATION

Israel AGRANAT*, Mordecai RABINOVITZ, Henry SELIG, and Chun-Hsu LIN

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

Phenanthrene reacts with xenon difluoride without HF initiation and in an open system to give fluorine substitution and addition products; 9-fluorophenanthrene is isolated in 33% yield.

Direct methods for the introduction of a fluorine atom into polycyclic aromatics are still in their infancy. Xenon difluoride has been shown to act as an efficient and selective fluorine substitution agent for simple aromatic compounds, both in solution and in the vapor phase.[1-4] It has been categorically stated that HF is a sine qua non for the reaction to proceed.[1b,5] We report that in the polycyclic aromatic series, e. g., phenanthrene, the direct fluorination by XeF_2 proceeds without HF initiation, effecting not only substitution at various positions, but also fluorine addition.

The reaction of XeF_2 and phenanthrene was carried out in the vacuum line system in dichloromethane solution, under strictly anhydrous conditions, taking painstaking care to avoid initial presence of HF. Comparable results were obtained in the presence of HF or in an open system. The ^{19}F n.m.r. spectrum of the crude reaction mixture contained the following absorption:[6] δ = 194.6 (relative area 21), 152.8 (6), 125.2 (33), 122.4 (3), 118.8 (8.0), 115.6 (12), 113.3 (5), 110.3 (7), and 107.9 (5). Careful column chromatography on silica, petroleum ether (40-60°C) serving as eluent, afforded 9-fluorophenanthrene as colourless needles, m.p. 51-53°C, in 33% yield. It was identified by the m.p. (lit.,[7] 51-52°C), elemental analysis, mass spectrum, and the chemical shift, multiplicity and coupling constants of the ^{19}F n.m.r. spectrum[6] (δ = 125.2, doublet of doublets (dd), J_1 = 11.9 Hz, J_2 = 2.0 Hz; lit.,[8-9] δ = 125.3, dd, J_1 = 11.8 Hz; J_2 = 2.0 Hz). The absorptions at 122.4, 115.6, 113.3, and 110.3 are reminiscent of 1-fluorophenanthrene (lit.,[8]

δ = 122.4), 2-fluorophenanthrene (lit.[8] δ = 115.3), 3-fluorophenanthrene (lit.,[8] δ = 113.5), and 4-fluorophenanthrene (lit.,[8] δ = 109.9), respectively. This analysis refers to the site of fluorination, and may apply as well to difluorophenanthrenes or to dimeric products.

The most significant absorption in the ^{19}F n.m.r. spectrum is the doublet of triplets at δ = 194.6 (J_1 = 50.1 Hz, J_2 = 15.6 Hz). The chemical shift and the pattern of this absorption, are indicative of a fluorine addition product, possibly 9,9,10-trifluoro-9,10-dihydrophenanthrene.[10] Indeed, the mass spectrum of the crude reaction mixture contained a prominent signal at m/e 234 due to a $C_{14}H_9F_3^{+\cdot}$ species. The mass spectrum indicated also the formation of difluoro- and tetrafluorophenanthrene derivatives. A yellow fluorination product, m.p. 180°C was isolated by column chromatography, but was not characterized. It should be noted that pyrene did not give any fluorine addition compound.[4]

In conclusion, the reaction of xenon difluoride with phenanthrene resulted in addition of fluorine (possibly across the 9,10 double bond), in predominant substitution by fluorine at the reactive 9-position, and in substitutions at less reactive positions.[11] The scope, generality and potential of this fluoroaromatic synthesis is further widened by the ability to carry it out in the absence of HF initiation, and under convenient experimental conditions.

References

1. (a) M. J. Shaw, H. H. Hyman, and R. Filler, J. Amer. Chem. Soc., 91, 1563 (1969); (b) ibid., 92, 6498 (1970); (c) J. Org. Chem., 36, 2917 (1971); (d) M. J. S. Shaw, J. A. Weil, H. H. Hyman, and R. Filler, J. Amer. Chem. Soc., 92, 5096 (1970).
2. D. R. Mackenzie and J. Fajer, J. Amer. Chem. Soc. 92, 4994 (1970).
3. T. C. Shieh, E. D. Feit, C. I. Chernick, and N. C. Yang, J. Org. Chem., 35, 4020 (1970).
4. Pyrene reacts with xenon difluoride to give predominantly 1-fluoropyrene, 2-fluoropyrene and dimeric products. See E. D. Bergmann, H. Selig, C.-H. Lin, M. Rabinovitz, and I. Agranat, J. Org. Chem., in the press (1975).
5. A breach in this 'state of the art' has very recently been reported in aryl oxygen compounds which undergo rapid fluorination with XeF_2 in the absence of HF initiation. See S. P. Anad, L. A. Quarterman, H. H. Hyman, K. G. Migliorese, and R. Filler, J. Org. Chem., 40, 807 (1975).
6. The ^{19}F n.m.r. spectra were recorded in dichloromethane at 94.1 MHz. ^{19}F chemical shifts (δ) are reported in p.p.m., upfield from CCl_3F.
7. M. A. Goldberg, E. P. Ordas, and G. Carsch, J. Amer. Chem. Soc., 69, 260 (1947).
8. (a) M. J. S. Dewar, R. C. Fahey, and P. J. Grisdale, Tetrahedron Letters, 343 (1963); (b) M. J. S. Dewar and J. Kelemen, J. Chem. Phys., 49, 499 (1968).
9. (a) K. D. Bartle and J. A. S. Smith, Spectrochimica Acta 23A, 1715 (1967). (b) K. D. Bartle, D. W. Jones, and R. M. Matthews, Tetrahedron, 27, 2701 (1969).
10. It has recently been quoted (M. Zupan, Ph.D. Thesis, University of Ljubljana, 1974) that xenon difluoride adds fluorine to 9,10-difluorophenanthrene to form 9,9,10,10-tetrafluoro-9,10-dihydrophenanthrene. See reference 8 in M. Zupan and A. Pollak, J. Org. Chem., 39, 2646 (1974).
11. Fluorination of naphthalene, anthracene and phenanthrene with xenon difluoride will be reported by R. Filler (Abstract of the 170th National Meeting, American Chemical Society, August 26-27, 1975).

(Received August 30, 1975)