

XENON DIFLUORIDE FLUORINATION. I.
ALIPHATIC ALKENES FLUORINATED BY A CONVENIENT BENCHTOP PROCEDURE

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We have found xenon difluoride to be a convenient fluorinating reagent with aliphatic alkenes when boron trifluoride etherate is employed as a catalyst. In a methylene chloride suspension, aliphatic alkenes of varying chemical structure produced different fluorinated derivatives. Our fluorination procedure required only such standard items as a dry box for storing and weighing the xenon difluoride, and a benchtop fume hood within which the fluorination reactions were conducted using conventional chemistry glassware.

Except for a gas phase investigation,^{2,3} the fluorination of aliphatic alkenes with xenon difluoride has not been defined. Recent xenon difluoride research has concentrated upon the fluorination of aromatic compounds that undergo fluorine substitution,⁴⁻¹⁰ or upon the fluorination of conjugated vinyl/acetylenic arenes that produce 1,2- or 1,1,2,2- vicinal fluoride derivatives respectively.¹¹⁻¹³ Such reactions were conducted in methylene chloride or diethyl ether solvent, and except for certain aryl ring systems,^{7,10} required anhydrous hydrogen fluoride as a catalyst. This catalyst negated using standard glassware equipment, and special Kel-F reaction vessels were required. Only a few laboratories have had access to custom stainless steel vacuum lines in which xenon difluoride has been handled and into which such Kel-F reaction vessels were generally integrated. Catalytic initiation with trifluoroacetic acid in place of hydrogen fluoride proved unacceptable since a 1-fluoro-2-trifluoroacetate derivative was produced as the major product instead of the difluoride.^{11,12}

This paper reports the first results of aliphatic alkene fluorination with xenon difluoride in a heterogeneous solvent suspension. Our non-vacuum line procedure is discussed because it employed the first conventional handling techniques and standard chemical glassware used in xenon difluoride fluorinations. Boron trifluoride etherate was used as the reaction catalyst and circumvented the difficulties encountered in handling anhydrous hydrogen fluoride.¹⁴ This liquid catalyst was easily weighed into methylene chloride solvent prior to its introduction into the XeF_2 /alkene methylene chloride suspension. Xenon difluoride, if pure and kept dry offers handling problems no more complex than any other highly reactive inorganic reagents commonly used in routine organic synthesis. Of the three known xenon fluorides (XeF_6 , XeF_4 , XeF_2), xenon difluoride is the safest. Pure xenon difluoride does not form the very dangerous explosive xenon trioxide upon hydrolysis,¹⁵ and its hydrolysis rate is relatively slow.¹⁶ This reagent is an easily

handled solid at room temperature although its 4.55 torr vapor pressure at 25°C¹⁷ does require its use within a properly vented dry box and fume hood.

The alkene fluorinations were accomplished on a 2.0-2.1 millimole scale. The solid xenon difluoride¹⁸ was stored in a Fisher Scientific Co. Isolator/Lab dry box under dry nitrogen. It was weighed into a 35 ml 14/20 ground glass, single-necked, round bottom flask containing a teflon coated magnetic stir bar. The 35 ml flask was stoppered, and the dry box was purged three times with fresh nitrogen. The spent nitrogen was pumped directly into a fume hood exhaust. The stoppered flask was removed from the dry box, transferred to a benchtop fume hood, and submerged in a dry ice/acetone cooling bath.¹⁹ Within 15 seconds, the stopper was removed from the 35 ml flask and replaced with a 15 ml pressure-equalized addition funnel fitted with a packed drying tube. All ground glass joints were sealed with silicone grease. One equivalent of alkene was weighed into 2 ml methylene chloride;²⁰ then, the solution was transferred into the addition funnel. The alkene solution was added dropwise to the solid xenon difluoride over 5-10 minutes, and the resulting heterogenous suspension was stirred as soon as mechanically possible. Next, a 0.25 to 0.76 equivalent of boron trifluoride etherate was weighed into 2 ml of methylene chloride. Within 5-10 minutes after the alkene solution addition, the boron trifluoride etherate solution was transferred into the addition funnel and was added dropwise over 5-10 minutes to the alkene/XeF₂ suspension. The reaction was stirred at -78°C for 5½ to 6½ hours. Some solid xenon difluoride remained at this point; the amount varied depending upon the alkene reactant. The dry ice/acetone bath was packed once more with dry ice and was wrapped with towels for insulation. Overnight (15-16 hours) the bath gradually warmed toward ambient temperature and all solid xenon difluoride disappeared. The reaction solution was washed with 10 ml deionized water containing 0.25-0.46 g sodium fluoride. It was dried over anhydrous magnesium sulfate, and filtered. In vacuo solvent removal afforded the crude product(s) which was isolated, analyzed, and purified by gas-liquid partition chromatography on a 10 ft. by ¼ in. 10% SE-30 column packed with 80/100 mesh Chromasorb W. All products were identified by mass spectrum, ¹H nmr, and/or ¹⁹F nmr analyses.

Three aliphatic alkenes with varying chemical structures were fluorinated, and each displayed a unique interaction with xenon difluoride. Major products resulting from 1,1-difluoro and 1,2-difluoro addition were observed, and in one case, fluorine substitution occurred with an accompanying carbon-carbon double bond migration. No aliphatic alkene produced a mixture of 1,1-difluorinated and 1,2-difluorinated products as was observed in the less selective gas phase xenon difluoride fluorinations.^{2,3}

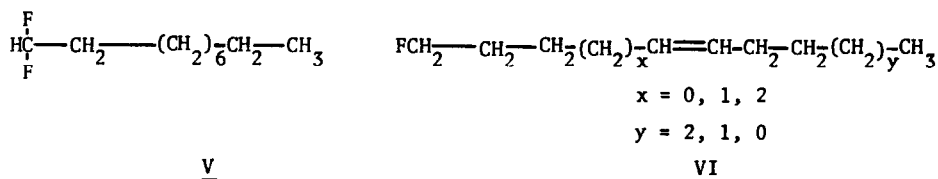
Reaction of 0.40 g 1,2-dibromoethene with xenon difluoride produced 0.29 g yellow oil that contained four fluorinated derivatives: 1,1-difluoro-2,2-dibromoethane I (59%), a nearly equal

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mixture of 1-fluoro-1-chloro-2,2-dibromoethane II and 1-fluoro-2-chloro-1,2-dibromoethane III (23%), and 1-fluoro-1,2,2-tribromoethane IV (18%). These product percentages remained essentially constant whether a 0.25 or 0.76 equivalent of the boron trifluoride etherate catalyst was used. The major product was the 1,1-difluoro derivative I formed by an apparent intramolecular 1,2-

bromine shift while compound IV formed from an intermolecular bromine migration. Products II and III reveal participation by the methylene chloride solvent. Such chlorine containing derivatives were observed only with the 1,2-dibromoethene reactant. Compounds II, III, and IV show that the chlorine and bromine species being generated during the reaction, compete favorably with the second fluorine species for addition to a monofluorodibromo intermediate. No fluorination resulted when diethyl ether was employed as the solvent.

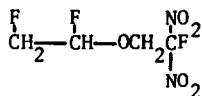
Fluorination of 0.29 g (96%) 1-decene yielded 0.32 g of yellow oil that contained two major components. The minor product was identified as 1,1-difluorodecane V and comprised 26% of the crude product. Its formation by a 1,2-hydrogen shift has been observed in the xenon difluoride gas phase reactions with aliphatic alkenes.^{2,3} The major product (48%) proved to be a trans-1-fluorodecene VI in which the vinyl protons were isolated from the terminal $-\text{CH}_2\text{F}$ group. Proton



nmr and mass spectral fragmentation appeared to rule out a 1-fluorodecene with the olefinic bond attached to the second, third, seventh, or eighth carbon atom. However, these spectra are not definitive for a 1-fluorodecene in which the olefinic bond resides at the fourth, fifth, or sixth carbon. Therefore, compound VI is either an isomeric mixture of the 4, 5, and 6-decenes or one single compound of the structure represented. Infrared spectrometry allowed assignment of the trans-isomer of VI by displaying a sharp absorption at 963 cm^{-1} .

While 1-decene afforded a major product derived from monofluoro substitution plus a minor product from 1,1-difluoro addition, and 1,2-dibromoethene provided a major product by 1,1-difluoro addition, a vinyl ether displayed a 1,2-difluoro addition product in excellent yield.

Fluorination of 0.40 g (95%) 2-fluoro-2,2-dinitroethyl vinyl ether produced 0.38 g yellow oil that contained one major component (79%) identified as 1',2'-difluoroethyl 2-fluoro-2,2-dinitroethyl ether VII. Compound VII was a colorless oil that displayed the reported 1,2-difluoro addition exhibited by conjugated vinyl arenes.^{11,12}



VII

While our results of xenon difluoride fluorination with aliphatic alkenes are preliminary, the initial structure of the alkene may influence the type of fluorinated derivative produced. Our safe, yet convenient, procedure should allow greater activity in fluorination studies, and as reaction conditions are refined, possible correlations between the initial alkene structure and type of fluorinated derivatives produced might significantly benefit the synthetic chemist. Additional studies into the scope and mechanism of these fluorinations are currently in progress.

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19. This reduces XeF_2 's vapor pressure prior to stopper removal.
20. The methylene chloride was treated prior to use by distillation over CaH_2 pellets and was stored over 4A molecular sieves.