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CYCLIZATION IN DEIODINATIVE FLUORINATION

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Abstract. Alkyl iodides **1-5** react with xenon difluoride with loss of iodide and incorporation of fluorine. A carbocationic intermediate undergoes cyclization with an internal olefinic function. © 1997 Elsevier Science Ltd.

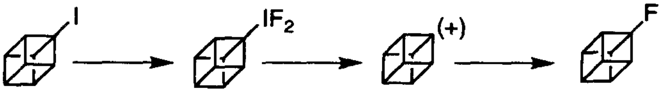
The fluorination of organic iodine compounds with xenon difluoride produces organic iodine difluorides. Aromatic iodine compounds thus yield aryl iodine difluorides that are useful as fluorinating agents (equation 1).[1,2]

$$\text{Ar-I} \xrightarrow{XeF_2} \text{Ar-IF}_2 + \text{Xe} \qquad (1)$$

Aliphatic iodine compounds produce alkyl iodine difluorides which decompose to give alkyl fluorine compounds. Janzen and coworkers [3,4,5] gave in 1973 the first report of the conversion of alkyl iodides to alkyl fluorides (deiodinative fluorination) which was later verified by Forster and Downs (equation 2).[6]

$$CH_3I \longrightarrow [CH_3IF_2] \longrightarrow CH_3F + IF \qquad (2)$$

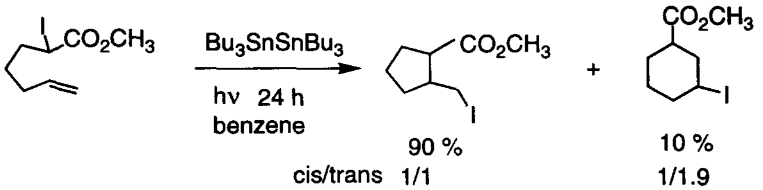
The studies were limited to the conversion of methyl iodide to methyl fluoride, but fluorination of isopropyl iodide gave unworkable mixtures. Della and Head in 1992 used deiodinative fluorination to prepare several strained bridgehead fluorides, such as fluorocubane.[7,8] Carbocations are postulated as intermediates in the formation of the fluorinated compounds (equation 3).[9,10]



(3)

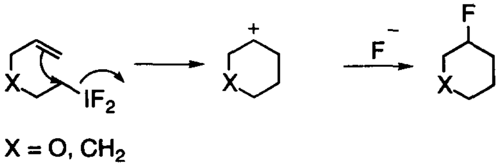
Recently we began a study of deiodinative fluorination with xenon difluoride with the goal of learning more about the nature of the reaction, particularly the involvement of free radicals or carbocations, and of extending the preparative scope of the reaction. Our initial studies involve the study competitive cyclization of some primary alkyl iodides and comparing the results with some known radical reactions, shown in Table I.

The reactions of the carboxylic acids with xenon difluoride are known to proceed by free radical intermediates[11,12] and show the usual 5-exo-trig selectivity expected for radical reactions.[13] Free radical reactions of alkyl iodides also favor 5-exo-trig selectivity as found by Curran and coworkers (equation 4).[14]



(4)

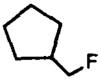
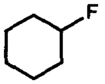
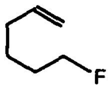
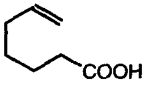
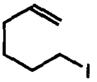
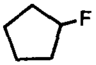
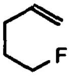
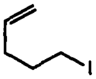
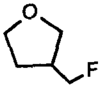
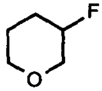
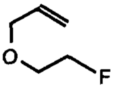
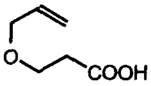
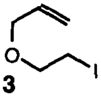
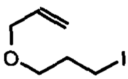
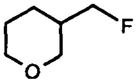
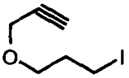
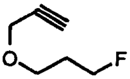
Iodo substrates **1** and **3** show 6-*endo-trig* selectivity over 5-*exo-trig*, and substrate **2** exhibits 5-*endo-trig* selectivity over 4-*exo-trig*. These results are consistent with carbocationic cyclizations and not radical cyclizations, as **1** and **3** would be expected to show mainly 5-*exo-trig* products if free radicals were involved (equation 5). Substrate **4** shows 6-*exo*--trig cyclization instead of 7-*endo-trig* cyclization that would provide a secondary carbocation. The observation of 6-*exo-trig* cyclization likely indicates participation by a complex ion intermediate. Finally the lack of cyclization seen in substrate **5** indicates both the disfavored strained in the intermediates required for cyclization and the unliklihood of forming a vinyl cation.



(5)

In a typical procedure the iodo substrate (0.01 mol) is dissolved in chloroform and treated with 0.01 mole of xenon difluoride (PCR, Inc.). The solution becomes purple in color. After washing with sodium bisulfite, the chloroform is concentrated and the products are identified by H and F NMR spectroscopy through comparison with known fluoro compounds prepared unambiguously by known methods.

TABLE I. CYCLIC PRODUCTS FROM DEIODINATIVE FLUORINATION

SUBSTRATE	PRODUCTS		
	 (5-*exo-trig*)	 (6-*endo-trig*)	 (F Substitution)
	25 %	0 %	75 %
 **1**	0 %	75 %	5 %
	 (4-*exo-trig*)	 (5-*endo-trig*)	 (F Substitution)
 **2**	0 %	80 %	15 %
	 (5-*exo-trig*)	 (6-*endo-trig*)	 (F Substitution)
	70 %	0 %	35 %
 **3**	0 %	70 %	30 %
 **4**	0 % (7-*endo-trig*)	 (6-*exo-trig*) 35 %	0 % (F Substitution)
 **5**	0 % (6-*endo-dig*)	0 % (7-*exo-dig*)	 (F Substitution) 10 %

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