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Thermal decomposition of alkenyliodonium tetrafluoroborates: a novel route to fluoroalkenes

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Abstract

Alkenyl(phenyl)iodonium tetrafluoroborates dissolved in chloroform, or in the solid state, decompose thermally at 60°C to yield fluoroalkenes and iodobenzene as major products via an S_N1- or S_N2-type reaction within the ion pair of the substrates.

Keywords: fluorine and compounds; pyrolysis; hypervalent elements; carbenium ions.

Alkenyliodonium salts undergo a variety of reactions owing to the high nucleofugality of the iodonio group.[1,2] The reactions include unimolecular as well as bimolecular nucleophilic substitutions and eliminations.[1b] The unimolecular reactions involve vinylic cations as intermediates which yield substitution and/or elimination products via trapping by a nucleophile/base[2–4] while the bimolecular (S_N2) reactions afford inverted nucleophilic substitution products.[5] We have found that the tetrafluoroborate salts of alkenyl(phenyl)iodonium compounds decompose thermally to give fluoroalkenes in the absence of any added nucleophile or base. Depending on the structure of the substrates, fluoroalkenes of inverted, retained, or scrambled configuration are produced. The reaction very likely takes place through an S_N1- or S_N2-type mechanism with the tetrafluoroborate anion acting as the fluoride donor. The reaction provides a novel route to fluoroalkenes from alkynes or other haloalkenes that can be converted into the iodonium salts via alkenylsilane, stannane, or boronic acid derivatives.[1a,6]

The thermolysis of the β-alkyl substituted (*E*)-1-alkenyl(phenyl)iodonium tetrafluoroborates **1a–c** dissolved in chloroform (or $CDCl_3$) at 60°C for 34–40 h yields 1-fluoro-1-alkenes (**2**), 1-alkynes (**3**) and iodobenzene as products (Eq. (1)). The yields summarized in Eq. (1) are percentages, determined by GC, and/or relative amounts (in parentheses), determined from ^1H NMR spectra of the reaction mixtures in $CDCl_3$.

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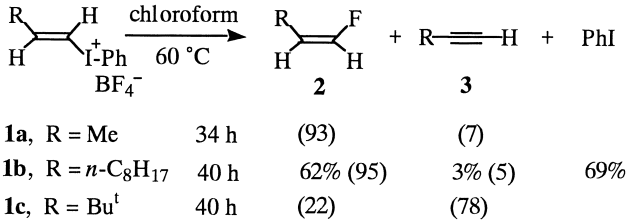
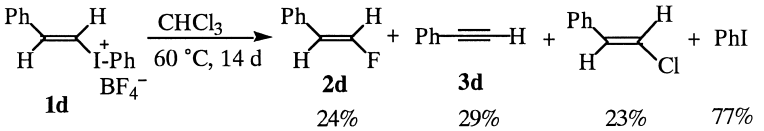


1a, R = Me	34 h	(93)	(7)	
1b, R = *n*-C_8H_{17}	40 h	62% (95)	3% (5)	69%
1c, R = Bu^t	40 h	(22)	(78)	

(1)

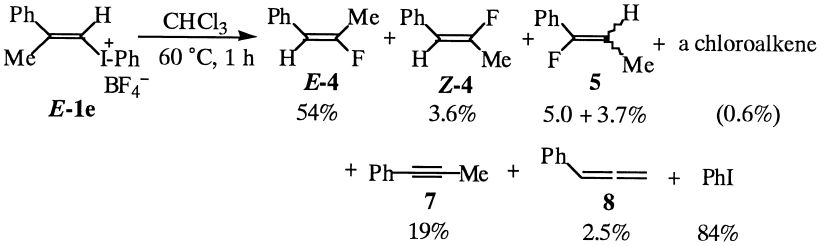
The stereochemistry of the fluoroalkenes **2a–c** was determined to be *Z* in all cases on the basis of the *trans* H-F, vicinal H-F and *cis* H-H couplings of about 45, 85, and 5 Hz in the ^{1}H NMR spectra,[7] respectively. No *E* isomers were detected. Thus, the substitution occurs exclusively by inversion of configuration, probably via the in-plane S_N2 pathway. For compounds **1a** and **b** elimination is a minor reaction, but for the *t*-butyl substrate **1c** the major product is alkyne **3c**. A similar trend has been observed for the in-plane S_N2 substitution of these iodonium salts by chloride and bromide ions.[5,8]

In contrast, the β-phenyl substituted (*E*)-styryl(phenyl)iodonium tetrafluoroborate **1d** gave (*E*)-1-fluoro-2-phenylethene (**2d**)[9] as well as (*E*)-1-chloro-2-phenylethene (Eq. (2)). The configurationally retained fluoroalkene **2d** must result from an intermediate vinylenebenzenium ion, similarly as in the reaction of **1d** with nucleophilic solvents.[3] The chloroalkene product must also be derived from the benzenium intermediate that attacks a chlorine atom of the solvent chloroform. Abstraction of a solvent chlorine atom by unstable carbenium ions was observed during dediazotization of arenediazonium ions[10] and photosolvolysis of iodoalkenes.[11] The formation of the chloroalkene in the thermal decomposition of **1d** may be considered as supporting evidence for the formation of a cationic intermediate. It should be noted that no chloroalkenes were detected during the thermolysis of 1-alkenyliodonium tetrafluoroborates **1a–c** and that these compounds afforded only the inverted fluoroalkenes.

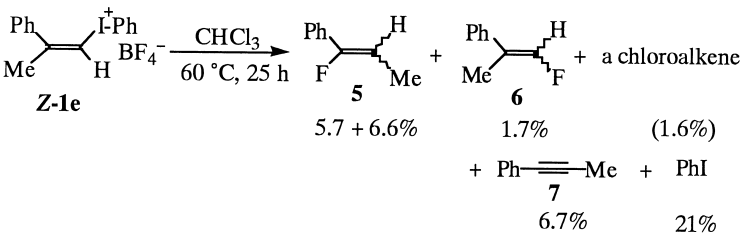


(2)

The thermolysis of (*E*)- and (*Z*)-2-phenyl-1-propenyl(phenyl)iodonium tetrafluoroborates *E*-**1e** and *Z*-**1e** in chloroform gave extensively rearranged fluoroalkenes and elimination products together with a small amount of a chlorine containing product (Eqs. (3) and (4)).[12] The reaction of the *E* isomer *E*-**1e** is much faster than that of *Z*-**1e** and the product distributions are strikingly different. Similarly different product distributions have been observed in the solvolysis of *E*-**1e** and *Z*-**1e**.[14]

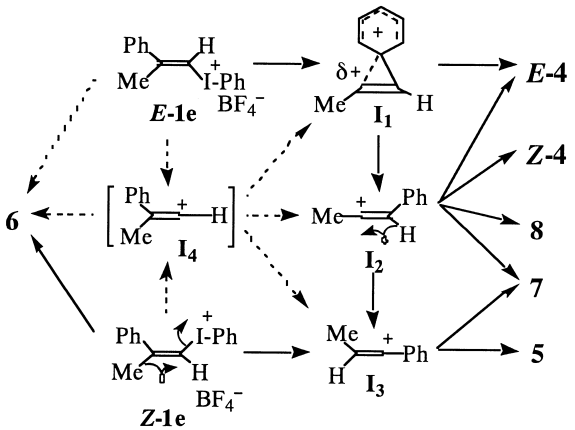


(3)



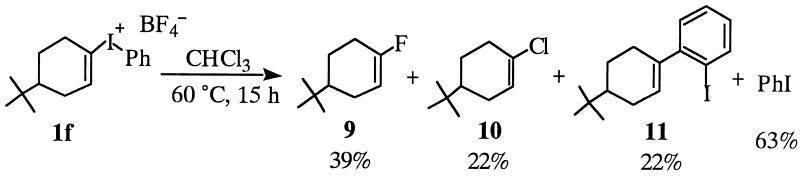
(4)

The results conform to reaction pathways involving phenyl and methyl participation for *E*-**1e** and *Z*-**1e**, respectively, and ensuing 1,2-hydride shift in a vinylic cationic intermediate as illustrated in Scheme 1. The major product *E*-**4** formed from *E*-**1e** is the result of trapping of the unsymmetrical vinylenebenzenium ion intermediate $\mathbf{I}_1$. The unbridged α-methylvinyl cation $\mathbf{I}_2$ is also a possible intermediate which leads to *E*-**4** and *Z*-**4**, as well as to the elimination products, **7** and **8**, by deprotonation. Cation $\mathbf{I}_2$ further rearranges by a 1,2-hydride shift to the α-phenylvinyl cation $\mathbf{I}_3$ which affords **5** and phenylpropyne **7**. The heterolytic C-I bond cleavage of *Z*-**1e** occurs with methyl participation and also results in the phenyl-stabilized cation $\mathbf{I}_3$. Further rearrangement of $\mathbf{I}_3$ is not possible because it is the most stable ion among isomeric vinylic cations.[15] The unrearranged fluoroalkene **6** must be formed directly from *Z*-**1e** via an S_N2 reaction. If the primary vinylic cation $\mathbf{I}_4$ were involved, more rearranged products would have been formed.



Scheme 1.

4-*t*-Butyl-1-cyclohexenyl(phenyl)iodonium tetrafluoroborate (**1f**) gave the corresponding fluorocyclohexene **9** together with considerable amounts of chlorocyclohexene **10** and *o*-(cyclohexenyl)-iodobenzene **11** (Eq. (5)). The products can be accounted for by the reaction of an intermediate cyclohexenyl cation: its trapping with tetrafluoroborate affords the fluorocyclohexene **9**, its attack on a chlorine atom of the solvent leads to the chlorocyclohexene **10**, and internal return within its ion-molecule pair with iodobenzene gives the Friedel–Crafts product **11** of *ortho* orientation. Product **11** was also obtained in the solvolysis of **1f**.[2]



(5)

The thermal reactions of **1b**, **d** and **f** were also examined in the solid state or in a suspension in *n*-hexane. The results are largely the same as those obtained in chloroform except for the formation of chloroalkenes. On the other hand, the reaction in acetonitrile afforded essentially no fluoroalkenes (only 0.5% **2d** from **1d** and no **2b** from **1b**). Effects of added salts are also dramatic: Addition of 0.1 mol dm^{-3} of tetrabutylammonium perchlorate completely inhibited formation of fluoroalkene in the chloroform reaction, while added tetrabutylammonium tetrafluoroborate barely affected the yield of fluoroalkene. These results strongly suggest that the formation of fluoroalkene occurs within the undissociated ion pair of the substrate iodonium salts, and the dissociated iodonium ion does not undergo the fluorination reaction.

The fluoride donor of this reaction is the paired tetrafluoroborate ion and not a fluoride ion generated therefrom, since fluoride ion induces exclusively α-elimination of 1-alkenyliodonium salts owing to its basicity (pK_a of HF = 3.17).[5] The present reaction resembles the Schiemann reaction of arenediazonium tetrafluoroborates yielding fluoroarenes[16] where also the counter anion has been concluded to be the direct fluoride donor.[10]

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8. The reaction of **1c** with chloride and bromide ions affords exclusively **3c** by β-elimination.[5c] The by-products **3** of the thermolyses of **1a**–**c** presumably arise from α-elimination induced by fluoride ion.[5]
9. The authentic sample was prepared according to Cox, D. G.; Gurusamy, N.; Burton, D. J. *J. Am. Chem. Soc*. **1985**, *107*, 2811.
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12. 1-Phenylpropyne (**7**)[13a] and phenylallene (**8**)[13b] were compared with authentic samples. The major product from *E*-**1e** was assigned as *E*-**4** (cf. Ref. 9) on the basis of its ^{1}H NMR [δ 2.11 (d, $J=18$ Hz, 3H), 6.18 (d, $J=21$ Hz, 1H)]; *Z*-**4** has the same MS spectrum as *E*-**4**. The structures of the other fluoroalkenes with a molecular peak of $m/z=136$ obtained from both *E*-**1e** and *Z*-**1e** (i.e. **5** and **6**) were tentatively assigned based on their GC–MS patterns. The chlorine containing product of $m/z=152/154$ (chloroalkene) was also detected by GC–MS.
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15. Formation of a more stable allylic cation ($PhCH{=}CHCH_2^+$) is in principle possible via a 1,2-hydride shift from $\mathbf{I}_2$, but the barrier for this process is quite high.[4b]
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