ORGANIC
LETTERS

2000
Vol. 2, No. 21
3359−3360

Rearrangement of Phenylethenes on Reaction with Iodine–Xenon Difluoride

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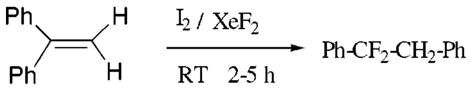
Received August 11, 2000

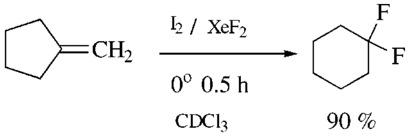
ABSTRACT



Phenyl-substituted ethenes react with iodine and xenon difluoride to provide difluorinated products. Iodofluoro intermediates react with xenon difluoride to produce transient iodine difluoride species that lose IF and F^- and produce carbocations.

Organic iodine compounds react with xenon difluoride to produce organoiodine difluorides that undergo transformations to organofluorine compounds. The reactions occur through mechanistic paths that involve carbocations.[1−10] In a study of the rearrangements that occur when organoiodine compounds are treated with xenon difluoride, we found that alkenes can be treated with iodine and xenon difluoride, Shellhamer's reagent,[11] to produce intermediate organoiodine compounds that undergo rearrangement on reaction with the xenon difluoride as exemplified in Scheme 1.[12,13]

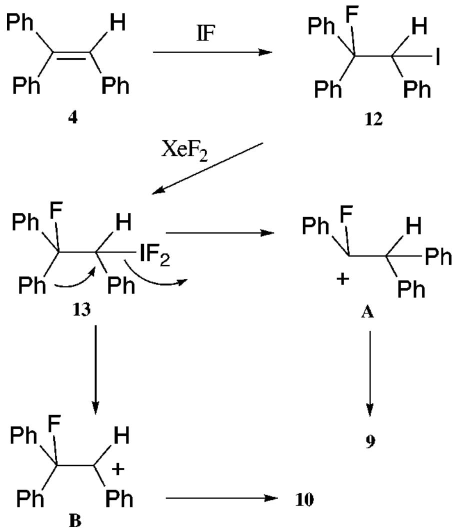
Scheme 1



In this Letter, we report a continuation of our studies on the reactions of I_2/XeF_2 alkenes that contain phenyl substituents.[14] The substrates and their reaction products are shown in Table 1.[15]

The mechanistic course of the reaction can be rationalized as shown in Scheme 2 with triphenylethene (**4**) as the model substrate. The alkenes react with iodine fluoride generated from the reaction between xenon difluoride and iodine in a

Scheme 2



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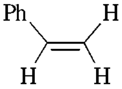
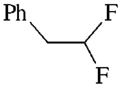
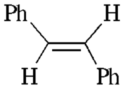
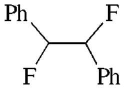
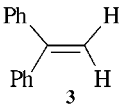
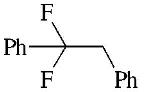
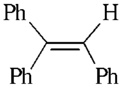
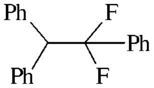
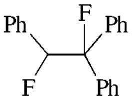
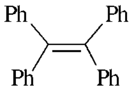
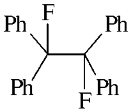
10.1021/ol006450d CCC: $19.00

Table 1

Substrate	Product(s)	Yield
 **1**	 **6**	50 %
 **2**	 **7** syn and anti	75 %
 **3**	 **8**	55 %
 **4**	 **9**	40 %
	 **10**	35 %
 **5**	 **11**	60 %

regioselective process that places the fluorine atom at the site of the more stable carbocation to produce the intermediate iodofluorinated intermediate **12**. Intermediate **12** reacts with a second equivalent of xenon difluoride to produce the iodine difluoride intermediate **13**. Similar intermediates have been postulated in earlier research.[12] The intermediate **13** loses IF and F^- with rearrangement to produce carbocation **A** or without rearrangement to produce carbocation **B**. The carbocations react with the fluoride ion to produce the final products. Carbocation stability likely governs the final product(s) produced. In all cases where rearrangement is observed (**6**, **8**, **9**), a fluorine-stabilized carbocation intermediate helps to drive the rearrangement.

In conclusion, the results show that unusual fluorinated products can be obtained in moderate to good yields by a relatively simple process that proceeds by predictable mechanistic routes.

Acknowledgment. We thank the National Science Foundation (RUI) and the Petroleum Research Fund (Type B) for support of this research.

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(14) Iodine (0.3 mmol) is added to the alkene (0.3 mmol) in 2 mL of $CDCl_3$ at room temperature. XeF_2 (0.61 mmol) is added, and the mixture is stirred overnight. The purple reaction mixture is subjected to column chromatography on silica gel with hexanes−ethyl acetate eluent.

(15) All compounds were characterized by NMR and high-resolution MS analysis. Representative NMR data follow. Compound **6**: ^{1}H (TMS) δ 3.15 (CH_2, t of d, $J_{HF} = 17.4$ Hz, $J_{HH} = 4.5$ Hz), 5.85 (CH, t of t, $J_{HF} = 57$ Hz, $J_{HH} = 4.5$ Hz), 7−7.6 (aromatic); ^{19}F (TFA) −39.2 (m); MS calcd 142.0594 amu, obsd 142.0580. Compound **7**: ^{1}H δ 5.7 (CH, partial d of d), 6.6−7.8 (aromatic); ^{19}F −109 (m), −110.4 (m); ^{13}C δ 94 (d of d), 96 (d of d), 127−132 (aromatic); MS calcd 220.1064, obsd 220.1069. Compound **8**: ^{1}H δ 3.36 (t,CH_2, $J = 18$ Hz), 6.9−7.6 (aromatic); ^{19}F −19.2 (t,CF_2, $J = 18$ Hz); ^{13}C 45.9 (t, CH_2, $J_{CF} = 11$ Hz), 121.9 (t, CF_2, $J_{CF} = 240$ Hz), 130−140 (aromatic); MS calcd 220.1064, obsd 220.1051. Compound **9**: ^{1}H δ 4.61 (t, CH, $J_{HF} = 16.9$ Hz), 7−7.8 (aromatic); ^{19}F −20.9 (d, CF_2, $J_{HF} = 16.9$ Hz); ^{13}C 59 (t, CH, $J_{CF} = 13$ Hz), 130−140 (aromatic); MS calcd 294.1221, obsd 294.1200. Compound **10**: ^{1}H δ 6.2 (dd, CH, $J_{HFgem} = 30$ Hz, $J_{HFvic} = 9$ Hz), 7.8 (aromatic), ^{19}F −83.7 (m, CF), −105.4 (d of m, CHF); ^{13}C 98.1 (dd, CHF, $J_{CF\ gem} = 216$ Hz, $J_{CF\ vic} = 21$ Hz), 106.1 (dd, CF, $J_{CF\ gem} = 142$ Hz, $J_{CF\ vic} = 21$ Hz), 120−130 (aromatic); MS calcd 294.1221, obsd 294.1249. Compound **11**: ^{1}H δ 6.9−7.4 (aromatic); ^{19}F −73.0 (s, CF); ^{13}C 99.0 (d,d CF, $J_{CFgem} = 190$ Hz, $J_{CFvic} = 30.4$; MS calcd 349.9997, obsd 349.9984.