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# Hydroarylation of 1-Aryl-2-Halogeno-3,3,3-Trifluoropropenes in CF<sub>3</sub>SO<sub>3</sub>H. Regioselective Approach to Trifluoromethylated Diarylethanes and Ethenes

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Abstract: The reaction of 2-halogeno-2-CF<sub>3</sub> substituted styrenes [ArCH=C(X)CF<sub>3</sub>, X = F, Cl, Br] with the superacid TfOH resulted in 100% regioselective formation of the corresponding benzyl cations [ArHC<sup>+</sup>–CH(X)CF<sub>3</sub>]. Subsequent reaction of these electrophilic species with arenes [Ar'H] afforded diastereomeric 1,1-diaryl-2-halogeno-3,3,3-trifluoro propanes [Ar(Ar')CH–CH(X)CF<sub>3</sub>] in high yields (up to 96%). The obtained halogenopropanes were easily transformed to the corresponding trifluoromethylated diarylethenes [Ar(Ar')C=CCF<sub>3</sub>] in yields of up to 95% by dehydrohalogenation using base. The elimination of chlorides and bromides using the KOH-ethanol system proceeds *via* an E2 elimination, whereas in the case of fluorides an E1cb elimination most probably takes place as the major reaction path.

### **Graphical abstract**:



1

Organofluorine compounds are of a great importance for chemistry, biology, medicine, nanotechnology, and material science. The trifluoromethylated fragment is a valuable structural unit, which is often present in pharmaceuticals, agrochemicals, and functionalized organic materials (Figure 1).<sup>1</sup>



Figure 1. Practically valuable molecules containing a CF<sub>3</sub>-alkene group.

Several approaches have been developed for the synthesis of CF<sub>3</sub>-alkenes.<sup>2</sup> Such alkenes are involved in various useful transformations: reactions with nucleophiles,<sup>3</sup> aryl halides,<sup>4</sup> silanes,<sup>5</sup> organoboron derivatives,<sup>6</sup> organolithium compounds,<sup>7</sup> enamines,<sup>8</sup> enolates,<sup>9</sup> and terminal alkynes,<sup>10</sup> oxidative cyclization with aldehydes,<sup>11</sup> as well as other reactions.<sup>12</sup> Trifluoromethylated alkenes can be used for the synthesis of polymers.<sup>13</sup> However, there are only two literature examples of superacidic activation of CF<sub>3</sub>-substituted alkenes.<sup>14</sup> To the best of our knowledge such reactions with trifluoromethylated alkenes bearing additional halogens are unknown. The presence of a halogen atom (F, Cl, Br) in the structure can be important for cation stabilization *via* formation of cyclic halonium cations. Such species are well recognized classical intermediates of many electrophilic reactions. The stability of halonium ions is decreased from heavy to light halogens. Iodonium and bromonium salts can be isolated, but the first evidence of fluoronium cations in solution was only demonstrated in 2013.<sup>15</sup>



Scheme 1. Protonation of alkenes 1 followed by the Friedel-Crafts alkylation of arenes

Based on our recent works on the transformations of  $CF_3$ -substituted alkynes,<sup>16</sup> carbonyl compounds,<sup>17</sup> and allyl alcohols<sup>18</sup> under the action of Brønsted or Lewis (super)acids, we extended this study to the reaction of trifluoromethylated styrenes bearing an additional halogen atom with various arenes under superelectrophilic activation. Due to the acceptor character of the  $CF_3$  group, protonation of alkene **1** should proceed with 100% regioselectively at the C<sup>2</sup> carbon to afford benzyl cation **A**, which may also exist as halonium ion **B** (Scheme 1). These species may participate in the Friedel-Crafts alkylation of arenes leading to trifluoromethylated diarylethane **2**, as products of the hydroarylation of the C=C bond of starting alkene **1**. The reaction of halonium ion **B** with nucleophiles (arenes) should be stereoselective, while contrary to that, a loss of stereoselectivity should be observed in the reaction of open cation **A** because nucleophilic attack can proceed from both sides of such a carbocation.

Starting 1-aryl-2-halogeno-3,3,3-trifluoro propenes **1a-l** (see Tables 1, 2) were synthesized by catalytic olefination from the corresponding arylaldehydes and 1,1,1-trifluoro-2,2,2-trihalogenoethanes.<sup>2a-c</sup>

We investigated the activation of alkenes **1** bearing various substituents on the aromatic ring and different halogen substituents at the double bond with Brønsted acids in the presence of arenes. First, we tested the reaction of 1-phenyl-2-chloro-3,3,3-trifluoropropene **1a**. This alkene did not react with benzene using  $H_2SO_4$  or  $CF_3CO_2H$  and only proceeded in the stronger trifluoromethane sulfonic acid  $CF_3SO_3H$  (TfOH) affording **2a** as the product of hydrophenylation of **1a** in 86% yield (Table 1, entry 1). Similar reactions were observed for other arenes including toluene, isomeric xylenes, pseudocumene, anisole, veratrole, and even the less nucleophilic 1,2-dichlorobenzene (entries 2-9). The reaction with TfOH is general and gave the target compounds **2** in high yields.

	CF <sub>3</sub> R-ArH	$ R^{-Ar} \xrightarrow{CF_3} -$	KOH, EtOH reflux, 15 h	-Ar CF <sub>3</sub> F	Ph_CF <sub>3</sub> -Ar
	<b>1a</b> (Z/E 83 : 17)	<b>2a-j</b> D1 and D2		<i>(Z)-<b>3 a-j</b> (from D1)</i>	<i>(E)-</i> <b>3 a-j</b> (from D2)
entry	R–ArH <sup>a</sup>	R (in 2, 3)	2 (yield, %)	<b>3</b> (yield, %)	ratio of D1/D2 for <b>2</b> and <i>Z</i> / <i>E</i> for <b>3</b>
1	benzene <sup>b</sup>	Н	<b>2a</b> (86)	<b>3a</b> (89)	_
2	toluene <sup>c</sup>	4-Me	<b>2b</b> (91)	<b>3b</b> (72)	37:63

2c (91)

2d (66)

2e (89)

**3c** (87)

3d (85)

3e (79)

 $3, 4-Me_2$ 

 $2,4-Me_2$ 

2,5-Me<sub>2</sub>

3

4

5

o-xylene<sup>c</sup>

*m*-xylene<sup>c</sup>

*p*-xylene<sup>*c*</sup>

Table 1. Hydroarylation of  $CF_3$ -alkene 1a in TfOH and dehydrochlorination of compounds 2a-j using the KOH-ethanol system

4	-		
		,	
		,	

53:47

29:71

67:33

6	pseudocumene <sup>c</sup>	2,4,5-Me <sub>3</sub>	<b>2f</b> (73)	<b>3f</b> (74)	53: 47
		2,3,5-Me <sub>3</sub>	<b>2g</b> (14)	<b>3g</b> (15)	50: 50
7	$1,2\text{-}\mathrm{Cl}_{2}\mathrm{C}_{6}\mathrm{H}_{4}{}^{b}$	3,4-Cl <sub>2</sub>	<b>2h</b> (22)	<b>3h</b> (89)	83 :17
8	anisole <sup>c</sup>	4-MeO	<b>2i</b> (70)	<b>3i</b> (87)	42: 58
9	veratrole <sup>c</sup>	3,4-(MeO) <sub>2</sub>	<b>2j</b> (43)	<b>3j</b> (86)	40: 60

<sup>*a*</sup>Molar ratio **1a** : arene 1: 5, for benzene 1 : 17. <sup>*b*</sup> r.t., 1 h. <sup>*c*</sup> 0 °C, 2 h.

Lower yields were observed in the case of 1,2-dichlorobenzene (entry 7) due to significant polymerization of the starting alkene **1** according to <sup>1</sup>H NMR data. The reaction was also highly regioselective in terms of arene selectivity. The carbocation formed attacks only the *para*-position of the substituted arenes, demonstrating the high steric demand of the electrophilic species formed (see, for instance, Table 1, entries 2, 3, 8). Also quite important was the stereochemical result of the reaction. The starting alkene **1a** had a 83 : 17 *Z/E* ratio. However, in all cases we observed the formation of a mixture of two diastereomers of **2b-j** (D1 and D2) in variable ratios ranging from 50 : 50 (1:1) up to 83:17 (5:1). These diastereomeric products have different (*R*)-, (*S*)- configurations of atoms C<sup>1</sup> and C<sup>2</sup>: D1 (*IRS*, *2RS*) and D2 (*ISR*, *2RS*) (Table 1, entries 2-9). In all <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra two sets of separate signals for each diastereomer **2b-j** were observed (see ESI). This data shows that the participation of chlorine in the stabilization of the formed cation is either not observed or only takes place to a very low extent. Therefore, the most probable carbocationic intermediate formed under the reaction conditions exists in the open form as the **A** type species (Scheme 1).

To elucidate the exact structure of the diastereomers we carried out dehydrochlorination of compounds **2** to give alkenes **3** by heating at reflux in KOH/ethanol for 15 h (Table 1). The *Z/E*-ratios of the formed alkenes **3** was the same as that of the D1/D2 ratios of their precursors **2**. According to these stereochemical results we can conclude that the transformation of **2** into **3** proceeds as an E2 elimination. *Z*-Alkenes **3** were formed from diastereomers D1 (*1RS,2RS*) and *E*-isomers **3** were obtained from diastereomers D2 (*1SR,2RS*), as depicted in Scheme 2 with the use of Newman projections. The configuration of the *Z*- and *E*-isomers of **3** can be easily elucidated using <sup>1</sup>H NMR spectra. The *E*-isomers of **3** have the vinyl proton signal low field shifted compared to the vinyl proton of the *Z*-isomer, as previously reported.<sup>16</sup> Based on these spectral data, we were able to determine the *Z/E*-stereochemistry of the formed alkenes **3** and elucidate the structures of the diastereomeric precursors, D1 and D2, of **2**.



Scheme 2. Newman projections of 2 and transformation of 2 into 3.

Next, the reactions of a series of alkenes 1b-l containing various aryl substituents and halogens (X = F, Cl, Br) with benzene in TfOH were studied (Table 2). We found that the transformation was general. Analogous to the reactions of 1a (Table 1), superacidic activation of other trifluoromethylated alkenes 1 led to formation of trifluoromethylated diarylethanes 2 in high yield (Table 2). Chloro- (X = Cl) **2b-l** and bromo- (X = Br) **2m-o** derivatives were converted into the corresponding alkenes 3 (Table 2, entries 1-7) by treatment with KOH in ethanol. This allowed the determination of the structures of diastereomers of compounds 2b,i,k-o. Dehydrobromination proceeded smoothly even at r.t. (Table 2, entries 5-7). Dehydrofluorination required harsher conditions (KOH, reflux, ethanol, 20 h), and in the case of compound 2s, gave alkene 3i with a Z/Eratio of 1:1, despite the initial ratio of diastereomers for 2s being 1 : 2 (Table 2, entry 11). This meant that, due to the strong electron withdrawing properties of the  $CF_3$  and F substituents, elimination of HF from 2s, most probably, proceeded in accordance with an E1cb mechanism, rather than an E2 mechanism (contrary to the chloro- and bromo- compounds 2, X = Cl, Br). We found that dehydrofluorination of **2p-s** could be carried out stereoselectively using *t*-BuOK in THF, affording alkenes 3a,b,i,l in good yields with Z/E-ratios corresponding to that of D1/D2 for 2p-s (Table 2, entries 8-11).

Table 2. Hydrophenylation of  $CF_3$ -alkenes 1b-l in TfOH and the dehydrohalogenation of compounds 2b,i,k-s

	R-Ar X <b>1b-I</b>	$\frac{\text{DH}}{\text{Ph}} \stackrel{\text{R-Ar}}{\stackrel{1}{\text{Ph}}}$	CF →	<sup>F</sup> 3 base F	.−Ar CF <sub>3</sub> Ph (Z)- <b>3a,b,i,k,I</b> (from D1)	R−Ar Ph CF <sub>3</sub> ( <i>E</i> )- <b>3</b> a,b,i,k,I (from D2)
entry	alkene $(Z/E$ -ratio) <sup><i>a</i></sup>	R in Ar	X	2 (yield, %)	<b>3</b> (yield, %)	ratio of D1/D2 for           2 and Z/E for 3
1	<b>1b</b> $(83:17)^b$	3-Me	Cl	<b>2k</b> (78)	<b>3k</b> $(85)^{e}$	77:23

2	<b>1c</b> $(86:14)^c$	4-Me	Cl	<b>2b</b> (96)	<b>3b</b> (87 <sup><i>e</i></sup>	71:29
3	<b>1d</b> $(75:25)^d$	4-Cl	Cl	<b>2l</b> (91)	<b>3l</b> (85) $^{e}$	75 :25
4	<b>1e</b> $(91:9)^c$	4-MeO	Cl	<b>2i</b> (91)	<b>3i</b> (94) <sup><i>e</i></sup>	83 : 17
5	<b>1f</b> $(89:11)^b$	Н	Br	<b>2m</b> (88)	<b>3a</b> (89) <sup><i>f</i></sup>	_
6	$1g(75:25)^b$	4-Cl	Br	<b>2n</b> (76)	<b>31</b> $(95)^{f}$	67:33
7	<b>1h</b> (87: 13) <sup>c</sup>	4-MeO	Br	<b>20</b> (54)	<b>3b</b> $(87)^{f}$	53 : 47
8	<b>1i</b> $(97:3)^b$	Н	F	<b>2p</b> (78)	<b>3a</b> (90) <sup>g</sup>	-
9	<b>1j</b> $(97:3)^c$	4-Me	F	<b>2q</b> (67)	<b>3b</b> (88) <sup>g</sup>	59: 41
10	<b>1k</b> $(97:3)^d$	4-Cl	F	<b>2r</b> (92)	<b>3l</b> (92) <sup>g</sup>	56:44
11	<b>11</b> $(97:3)^b$	4-MeO	F	<b>2s</b> (90)	<b>3i</b> (93) <sup>g</sup>	33 : 67

<sup>*a*</sup>Molar ratio **1a** : arene 1: 5. <sup>*b*</sup>r.t., 1 h. <sup>*c*</sup>-10 °C, 0.5 h. <sup>*d*</sup>60 °C, 1 h.

<sup>*e*</sup>KOH, EtOH, reflux, 15 h. <sup>*f*</sup>KOH, EtOH, r.t., 20 h. <sup>*g*</sup>*t*-BuOK, THF, r.t. (or reflux), 2 d.

Some features of this hydroarylation reaction should be noted. The reaction is very sensitive to the nature of the halogen atoms on the double bond and substituents on the aromatic ring. For example, alkenes **1d** and **1k** (with X = CI and F) bearing an acceptor chlorine atom in the *para*-position of the aryl ring are hardly protonated using TfOH. These alkenes **1d** and **1k** interact with benzene only at an elevated temperature of 60 °C (Table 2, entries 3, 10). Other alkenes **1** containing electron donating substituents react smoothly at -10 °C or r.t. (Tables 1, 2). Polymethylated arenes such as mesitylene and durene do not participate due to the sensitivity of this reaction to steric hindrance from the two *ortho*-methyl groups in these arenes. Also, the key point of this reaction is the preservation of the  $C^2-X$  (X = F, Cl, Br) bond in compounds **2** under superacidic conditions. Usually this kind of carbon-halogen bond is easily cleaved in superacids,<sup>19</sup> however no cleavage of this bond is observed for substrates **2** due to the electron withdrawing influence of the neighboring CF<sub>3</sub> group.

In many cases the hydroarylation proceeds rather stereoselectively with predominant formation of one of the diastereomers D1 or D2 (see ratios of D1/D2 in Table 1, entries 2, 4, 5, 7, and Table 2, entries 1-4, 6, 11). The diastereomeric ratio most probably depends on steric factors. Despite not regulating the stereoselectivity of the reaction, data on the diastereomeric content of compounds 2 sheds light on the reactivity of cations A and B (Scheme 1). Thus, in the case of fluoroalkenes 1i-l (X = F) the stereoselectivity is poor and alkenes 1j-l with a Z/E- ratio of 97 : 3 led to compounds 2q-s with D1/D2 ratios ranging from 33-59 : 67-41 (Table 2, entries 9-11). Such a loss of stereoselectivity reveals that in the case of the fluoroderivatives a cyclic fluoronium ion cannot be postulated, and thus the diastereocontrol could only come from a cation of type A. For

brominated (X = Br) and chlorinated (X = Cl) substrates 1 the formation of halonium ions **B** is more probable.

It should be noted that alkenes 3 are structurally close to Panomifene, which is a well known anticancer drug (Figure 1). Therefore, the synthesis of such alkenes is of significant theoretical and practical importance.<sup>20</sup>

In conclusion, we have developed simple and highly efficient method for hydroarylation of double bond of 2-halogeno-2-CF<sub>3</sub> styrenes by their reactions with arenes in TfOH leading to 1,1-diaryl-2-halogeno-3,3,3-trifluoro propanes. The latter compounds can be transformed into 1,1-diaryl-3,3,3-trifluoro propenes by dehydrohalogenation.

#### **Supporting Information**

Experimental details, compound characterization, and <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F NMR spectra.

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