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A Facile Preparation of Aryl Triflates. Decomposition of Arenediazonium Tetrafluoroborate Salts in Trifluoromethanesulfonic Acid

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The thermal or photochemical decomposition of arenediazonium tetrafluoroborate salts in trifluoromethanesulfonic acid, with or without organic bases such as pyridine, provides aryl triflates in high yields.

Perfluoroalkanesulfonic esters are useful synthetic reagents because of the eminent leaving group properties.[1-3] Aryl triflates (ArOTf) can be prepared in the reaction of phenols or their o-silyl derivatives with trifluoromethanesulfonic anhydride or trifluoromethanesulfonyl halides, respectively.[1,4] This procedure, however, is not applicable to the preparation of ArOTf bearing a hydroxyl group. Although arenediazonium salts (ArN_2BF_4) are known to give the corresponding ArOTf in trifluoromethanesulfonic anhydride,[5] this reaction is accompanied by the formation of a considerable amount of aryl fluorides (ArF) and does not occur with ArN_2BF_4 bearing NO_2. We have found a highly effective preparation of ArOTf by the thermal or photochemical decomposition of ArN_2BF_4 in trifluoromethanesulfonic acid (CF_3SO_3H).

The general reaction procedure is as follows. 1) Thermolysis: A solution of ArN_2BF_4 (3 mmol) dissolved in 5 mL of CF_3SO_3H (56.5 mmol) was heated at the temperature listed in Table 1. Then the reaction mixture was kept at this temperature for 1 h under stirring. 2) Photolysis: A solution of ArN_2BF_4 in CF_3SO_3H was irradiated with a high pressure Hg-lamp at 12 °C for 6 h. The resulting solution obtained by either of these procedures was quenched with ice-water. The products were separated from the crude mixture by column chromatography on silica gel. All products were fully characterized by spectroscopy.

As seen in Table 1, ArN_2BF_4 undergoes decomposition in CF_3SO_3H to afford ArOTf in good yields, together with a trace of ArF in some cases. Substituents in ArN_2BF_4 are not important with respect to the yields of ArOTf, while NO_2 at the ortho position retards the reaction somewhat. It is noteworthy that the aryl diazonium salts with a hydroxyl group produce the corresponding triflates in sufficient yields. The methoxyl and trifluoromethyl groups in the diazonium salts are partly hydrolyzed under the reaction conditions. However, use of trimethylamine or pyridine successfully inhibited the undesired hydrolysis.

The decomposition of ArN_2BF_4 in CF_3SO_3H was also induced photochemically to afford ArOTf efficiently and to depress the formation of undesired side products.

Table 1. Preparation of ArOTf from ArN_2BF_4

$XC_6H_4N_2BF_4$	Solvent	Temp/°C	Ar-OTf/%a)	Ar-F/%a)	Others/%
X = H	$(CF_3SO_2)_2O$	60-80	(3 :	1)b)	
"	CF_3SO_3H	80	93d)	trace	-
o-,m-,p-CH_3	"	90	73-75	trace	-
p-CH_3	$(CF_3SO_2)_2O$	60-80	(1 :	1)b)	
o-OH	CF_3SO_3H	130	92	0	-
m-OH	"	80	84	0	-
p-OH	"	140	80	0	-
o-Cl	"	160	79	0	-
m-Cl	"	90	80	0	-
p-Cl	"	90	74	0	-
"	$(CF_3SO_2)_2O$	60-80	(4 :	5)b)	
o-NO_2	CF_3SO_3H	170	33	0	-
m-NO_2	"	120	84	0	-
p-NO_2	"	100	84	0	-
NO_2c)	$(CF_3SO_2)_2O$	60-80	no reaction5)		
m-OCH_3	CF_3SO_3H	60	52d)	0	43d,e)
"	" + Et_3Nf)	60	89d)	trace	traced,e)
"	CF_3SO_3H	$h\nu$g)	82d)	trace	-
o-OCH_3	$(CF_3SO_2)_2O$	60-80	(1 :	2)b)	
m-CF_3	CF_3SO_3H	90	85e)	0	13h)
"	" + pyridinef)	90	89e)	trace	-
"	CF_3SO_3H	$h\nu$g)	81	trace	-

a) Isolated yields unless otherwise noted. b) The reported yields are 90-95% in total. Molar ratio.5) c) Nothing is specified in the report about the position.5) d) GLC yield. e) m-Hydroxyphenyl trifluoromethanesulfonate. f) CF_3SO_3H : NEt_3 (or pyridine) = 3 : 1 equiv/equiv. g) 500 W High Pressure Hg-lamp, 12 °C for 6 h. h) m-(Trifluoromethanesulfonyloxy)benzoic acid.

Consequently, the present procedure provides a facile synthesis of ArOTf from ArN_2BF_4.

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