Induced oxidative rearrangement of non-terminal alkynes by [fluoro(trifluoromethanesulfonyloxy)iodo]benzene to esters of 2-alkyl- and 2-arylalkanoic acids

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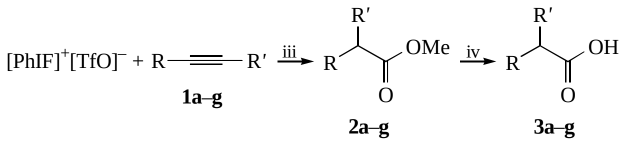
The oxidation of non-terminal acetylenes by [fluoro(trifluoromethanesulfonyloxy)iodo]benzene in methanol causes oxidative rearrangement to esters of 2-alkyl- and 2-arylalkanoic acids.

Hypervalent iodine reagents react with alkynes to give various products depending upon the type of reagent, the structure of alkynes and the reaction conditions. Terminal alkynes react with [hydroxy(tosyloxy)iodo]benzene to yield alkynyl iodonium tosylates,[1] which are important intermediates for the syntheses of alkynyl carboxylates,[2] phosphates[2] and triflates.[3] Reactions of (perfluoroalkyl)phenyliodonium salts with terminal alkynes yield a mixture of substitution and addition products.[4] Non-terminal alkynes are converted to α-diketones by oxidation with iodosobenzene in the presence of ruthenium,[5] while terminal alkynes afford carboxylic acids.[5] Oxidation of alkynyl ethers and alkynyl amines with PhIO in the presence of $\mathrm{Ru^{II}}$ catalysts yields α-ketoesters and α-ketoamides,[6] respectively. Bis-trifluoroacetoxyiodobenzene (PIFA) reacts with non-terminal alkynes to give α-diketones,[7] while terminal alkynes yield α-hydroxyketones.[7,8] The cleavage of alkynes to carboxylic acids has been accomplished using PIFA/C_6H_6/H_2O under reflux conditions.[9] Oxidative rearrangement of terminal and non-terminal alkynes by [hydroxy(tosyloxy)iodo]benzene affords carboxylic acid esters.[10]

Recently, a new approach was suggested for the one-pot generation of aryliodoso derivatives directly from iodoarenes.[11] The iodonium triflate with the general formula $[\mathrm{ArI^+F^-OTf}]$ is assumed to result from the oxidation of iodoarenes upon treatment with xenon fluorotriflate. It was shown that the reactions of these reagents with terminal acetylenes are accompanied with anti-addition to afford (*E*)-[β-(trifyloxy)alkenyl]-(aryl)iodonium triflates in moderate to excellent yields.[11]

In a continuation of our investigation on hypervalent iodine chemistry, we now report the results of reaction of [fluoro-(trifluoromethanesulfonyloxy)iodo]benzene with non-terminal alkynes in methanol. It is interesting to note that this reaction is accompanied by oxidative rearrangement of non-terminal alkynes to esters of alkyl and arylalkanoic acids (Table 1). A great attention directs towards the synthesis of arylalkanoic acids due to their anti-inflammatory properties.[10,12,13]

$$\mathrm{XeF_2 + HOTf \xrightarrow[-\,HF]{i} FXeOTf \xrightarrow[-\,Xe]{ii} [PhIF]^+[TfO]^-}$$



a R = Ph, R′ = Me
b R = Ph, R′ = Et
c R = R′ = Ph
d R = *p*-$NO_2C_6H_4$, R′ = Me
e R = *p*-$MeCOC_6H_4$, R′ = Me
f R = R′ = Et
g R = Pr, R′ = Me

Scheme 1 *Reagents and conditions*: i, CH_2Cl_2, –78 °C; ii, PhI, CH_2Cl_2; iii, MeOH; iv, aqueous NaOH, then 5% aqueous HCl.

Table 1 Oxidative rearrangement of non-terminal acetylenes with $[\mathrm{PhI^+F^-OTf}]$ in methanol.

Starting compound	Reaction time/h	Product	Yield (%)	Characteristic
1a	22	**3a**	52	n_D^{20} 1.5231[14]
1b	28	**3b**	42	mp 43–44 °C
1c	28	**3c**	47	mp 147 °C[14]
1d	28	**3d**	44	mp 89 °C[14]
1e	30	**3e**	53	mp 57 °C[15]
1f	25	**3f**	39	n_D^{20} 1.4129[14]
1g	25	**3g**	40	n_D^{20} 1.4142[14]

A likely mechanism for these oxidative rearrangements entails the initial formation of 2-methoxy-1-alkenyl(phenyl)iodonium triflates **A** analogous to the production of (2-trifyloxy-1-alkenyl)iodonium salts from terminal alkynes with $\mathrm{PhI^+F^-OTf}$ in non-hydroxylic solvents.[11] Michael addition followed by a 1,2-shift of the R group in **B** with dissociative reductive elimination of iodobenzene would ultimately afford **2a–g**.†

In summary, iodine(III)-induced oxidative rearrangement of non-terminal acetylenes by [fluoro(trifluoromethanesulfonyl-oxy)iodo]benzene offers an efficient procedure for the specific transformation of alkynes to alkyl- and arylalkanoic acids.

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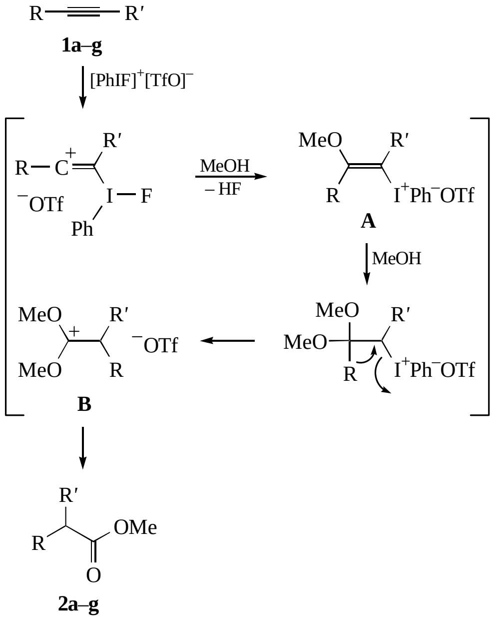

Scheme 2

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† *Typical procedure*. A solution of iodobenzene (1.3 mmol) in CH_2Cl_2 (5 ml) was added dropwise at –78 °C to a solution of FXeOTf (1.3 mmol)[16] in dry CH_2Cl_2 (20 ml). The mixture was stirred for 0.5 h at –78 °C. Next, an appropriate alkyne (10 mmol) was added dropwise to a solution of $[PhIF]^+[TfO]^-$ in CH_2Cl_2 at –78 °C. The mixture was allowed to warm to –30 °C, and the stirring was continued for 0.5–1 h. Then, the mixture was cooled to –78 °C, and methanol (15 ml) was added dropwise to the solution. After being warmed to room temperature over 3 h, the stirring was continued for 20–30 h. Next, the mixture was treated with a saturated $NaHCO_3$ solution. Extraction with CH_2Cl_2 (3×15 ml) followed by drying ($MgSO_4$) and concentration at a reduced pressure gave a mixture of ester **2a**–**g** and iodobenzene. The ester was purified by column chromatography on silica gel using heptane–diethyl ether (6:1) as an eluent. Hydrolysis in a 2 M NaOH solution yielded corresponding carboxylic acids **3a**–**g** in good yields. All known products were identified by the IR and ^{1}H NMR spectral data (Table 1).