Synthesis and nucleophilic substitution of allenyl(*m*-nitrophenyl)iodanes as a new propynyl cation-equivalent species: synthesis of propynyl ethers, esters, and amides

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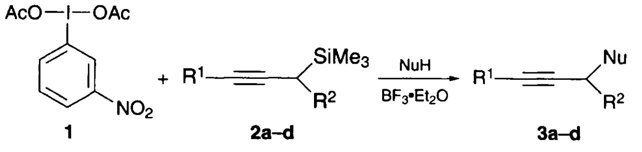
Treatment of diacetoxy(*m*-nitrophenyl)iodane with propynylsilanes in the presence of $BF_3{\cdot}Et_2O$ gives allenyl(*m*-nitrophenyl)iodanes, which act as propynyl cation-equivalent species and undergo regioselective nucleophilic substitution with alcohols, carboxylic acids and nitriles to give propynyl ethers, esters and amides.

We have reported [3,3]-sigmatropic rearrangement involving a hypervalent iodine atom in which allenyl(aryl)iodanes, generated by S_E2' reaction of aryliodanes with propynylsilanes in the presence of $BF_3{\cdot}Et_2O$, undergo a reductive iodonio-Claisen rearrangement at −20 °C in dichloromethane yielding *ortho*-propynyliodoarenes in good yields.[1] When a π-donor methoxy group was introduced to the aromatic ring of aryliodanes at the *ortho* or *para* position, this aromatic *ortho* iodonio-Claisen rearrangement of allenyl(aryl)iodanes competes with deiodinative ipso iodonio-Claisen rearrangement yielding ipso-substituted propynylarenes.[2] The *ortho vs.* ipso selectivity depends on the solvent basicity and the extent of normal *ortho* selectivity increases with increased solvent basicity.[3] In marked contrast, the presence of an electron-withdrawing nitro group at the *meta* position of allenyl(aryl)iodanes makes the reductive iodonio-Claisen rearrangement very difficult: for instance, no formation of rearranged products, 1-(2-iodo-4-nitrophenyl)- and 1-(2-iodo-6-nitrophenyl)oct-2-yne, was observed in the reaction of diacetoxy(*m*-nitrophenyl)iodane **1** with 1-(trimethylsilyl)oct-2-yne **2a** in dichloromethane and in this case *m*-nitroiodobenzene was obtained quantitatively. We report here nucleophilic substitutions of allenyl(aryl)iodanes, generated from the *m*-nitroiodane **1** by the reaction with propynylsilanes **2**, in alcohols, carboxylic acids and nitriles, which result in selective formation of propynyl ethers, esters and amides, respectively.

When **2a** was treated with an equivalent amount of the *m*-nitroiodane **1** in methanol (100 equiv.) in the presence of $BF_3{\cdot}Et_2O$ (1 equiv.), which activates **1** by coordination to the oxygen atoms of the ligands on iodine(III), at room temperature for 6 h, replacement of a trimethylsilyl group by a methoxy group was observed and oct-2-ynyl methyl ether **3a** (Nu = MeO) was obtained in 79% yield. While all of the oxidant, *m*-nitroiodane **1**, was consumed under these reaction conditions, a considerable amount of **2a** was recovered unchanged (18%). Use of 1.2 equiv. of **1** led to complete disappearance of **2a** and afforded **3a** (Nu = MeO) in 89% yield. A similar tendency was observed in the nucleophilic substitutions of propynylsilane **2a** in primary and secondary alcohols; in these cases, even if 1.2 equiv. of **1** were employed, more than 30% of **2a** was recovered. The yields of **3a** and the recovered **2a** are as follows: in EtOH, **3a** (Nu = EtO, 59%) and **2a** (33%); in PrOH, **3a** (Nu = PrO, 37%) and **2a** (32%); in Pr^{i}OH, **3a** (Nu = Pr^{i}O, 29%) and **2a** (62%); in Bu^{s}OH, **3a** (Nu = Bu^{s}O, 38%) and **2a** (48%). It appears that the amount of recovered propynylsilane **2a** increases in the sequence MeOH < primary alcohols < secondary alcohols. These results suggest the occurrence of some competing reactions, in which the oxidant **1** was involved but not the propynylsilane **2a**.

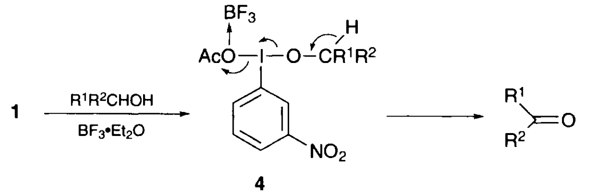
The reaction that competes with the nucleophilic substitution of **2a** was found to be the oxidation of alcohols to carbonyl compounds and their derivatives by the combination of *m*-nitroiodane **1** and $BF_3{\cdot}Et_2O$. For instance, reaction of **1** with a large excess of propanol in the presence of $BF_3{\cdot}Et_2O$ at 30 °C for 4 h gave 1,1-dipropoxypropane in 96% yield. Similar oxidation of Bu^{s}OH (30 °C/15 min) and cyclohexanol (30 °C/1.5 h) afforded butan-2-one and cyclohexanone in 92 and 93% yields, respectively. Furthermore, it was found that the relative rates of oxidation of primary to secondary alcohols with **1** follows the order PrOH < cyclohexanol < Bu^{s}OH. This BF_3-catalysed oxidation of alcohols with **1** probably involves a rapid ligand exchange on the hypervalent iodine of **1** with alcohols generating the alkoxyiodane **4**,[4] followed by a rate-limiting reductive elimination of *m*-nitroiodobenzene with concomitant α-C–H bond cleavage yielding carbonyl compounds,[5] both steps being catalysed by BF_3. A relatively large primary kinetic deuterium isotope effect (k_H/k_D = 4.84) observed in the reaction of cyclohexanol-α-[^{2}H] strongly indicates that the α-C–H bond cleavage is involved to a great extent in the rate determining step of the oxidation of alcohols.[6] Therefore, it seems reasonable to assume that the increased amounts of the recovered propynylsilane **2a** in the order of methyl < primary < secondary alcohols, as mentioned above, probably reflect the differences in dissociation energies of the cleaving α-C–H bonds of alcohols:[7] kcal mol^{-1}, $C\mathit{H}_3OH$ (94), $CH_3C\mathit{H}_2OH$ (93) and $(CH_3)_2C\mathit{H}OH$ (91).

Use of 2 equiv. of **1** led to the complete disappearance of **2a** in nucleophilic substitution with alcohols to afford high yields of propynyl ethers **3a**. The results are summarized in Table 1. Acetic acid also functions as a good nucleophile towards the generated allenyl(*m*-nitrophenyl)iodane; since the competing



a $R^1 = C_5H_{11}$, R^2 = H, **b** R^1 = c-C_6H_{11}, R^2 = H,
c $R^1 = C_{10}H_{21}$, R^2 = H, **d** R^1 = H, $R^2 = C_{10}H_{21}$

Scheme 1



Scheme 2

oxidation of the nucleophile does not proceed in this case, use of an equivalent amount of the oxidant **1** gave a high yield of propynyl acetate **3a** (Nu = AcO). α-Substituted propynylsilane **2d** similarly gave the substitution product **3d** selectively.

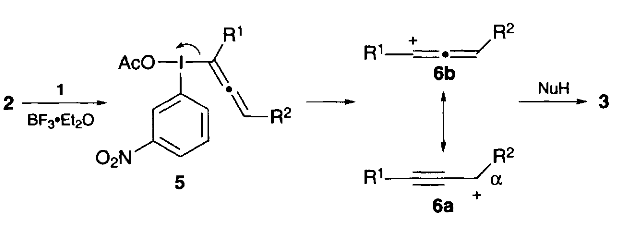
In addition, the reaction in acetonitrile afforded the propynyl amide **3a** (Nu = MeCONH) in 91% yield. Use of propionitrile or benzonitrile as a nucleophile, however, led to poor results, giving the amide **3a** (Nu = EtCONH or PhCONH) in less than 10% yield. Since hypervalent iodine(III) reagents have been used for direct conversion of carboxamides to amines although secondary and tertiary amides are less reactive than primary amides,[8] the low yields of the latter amide **3a** (Nu = EtCONH or PhCONH) might be attributed to the further reaction of this initially formed amide **3a** with **1**. Furthermore, it has been shown that relative rates of the reaction of amides ($RCONH_2$) with bis(trifluoroacetoxy)(phenyl)iodane yielding amines (RNH_2) are as follows: R (relative rate), Me (1) < C_5H_{11} (11) < Bu^t (62) < Pr^i (84).[9]

A plausible mechanism for the conversion of propynylsilanes **2** to propynyl ethers **3** (Nu = RO) by the reaction with **1** is given in Scheme 3. The initial formation of an allenyl(*m*-nitrophenyl)iodane **5** by BF_3-catalysed S_E2' reaction of aryliodane **1** with propynylsilane **2** and its follow-up collapse to propynyl cation **6** with reductive elimination of *m*-nitroiodobenzene seems most likely.[1,10] Similar intermediate propynyl carbocations have been generated by S_N1 solvolysis of allenyl halides in aqueous alcohols.[11]

Table 1 Nucleophilic substitutions of propynylsilane **2** using *m*-nitrophenyliodane **1**[a]

				Product **3**	
Silane **2**	Iodane **1** (equiv.)	NuH	*t*/h	Nu	Yield (%)[b]
a	1.2	MeOH	1.5	**3a** MeO	(89)
a	2.0	EtOH	2	**3a** EtO	(91)
a	2.0	PrOH	2.5	**3a** PrO	(90)
a	2.0	$C_9H_{19}OH$	24	**3a** $C_9H_{19}O$	(87)
a	2.0	Pr^{i}OH	2.5	**3a** Pr^{i}O	(86)
a	2.0	Bu^{s}OH		**3a**Bu^{s}O	(91)
a	2.0	Bu^{t}OH	16	**3a** Bu^{t}O	(88)
a	1.0	AcOH	2	**3a** AcO	(90)
a	1.2	MeCN	1.5	**3a** MeCONH	91
b	1.2	MeOH	2	**3b** MeO	68(72)
b	1.05	AcOH	2	**3b** ACO	63(74)
c	1.2	MeOH	2	**3c** MeO	68(85)
c	1.05	AcOH	2	**3c** AcO	77(78)
c	1.2	MeCN	3	**3c** MeCONH	49
d	1.2	MeOH	2	**3d** MeO	(63)
d	1.05	AcOH	2	**3d** AcO	56(63)
d	1.2	MeCN	3	**3d** MeCONH	60

[a] Reactions were carried in the presence of $BF_3{\cdot}Et_2O$ equivalent to **1** in a nucleophilic solvent (100 equiv.) at room temp. under nitrogen. [b] Isolated yields. Parenthesis are GC yields.



Scheme 3

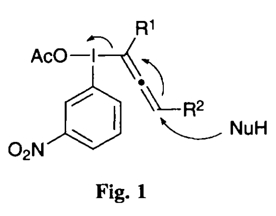


Fig. 1

We have reported that the phenyliodonio group is a remarkably good nucleofuge with a leaving ability 8 × 10^5 times greater than triflate, the so-called superleaving group,[12] and the leaving ability of the aryliodonio group increases with an increase in the electron-withdrawing ability of the ring substituent.[13] The leaving ability of the *m*-nitrophenyliodonio group can be evaluated from the reported Hammett ρ value for solvolysis of cyclohexenyl(aryl)iodonium tetrafluoroborates to be 16 times greater than phenyliodonio group. Thus, it seems reasonable to assume that the very high leaving ability of the *m*-nitrophenyliodonio group would be responsible for the selective collapse of allenyl(*m*-nitrophenyl)iodane **5** to propynyl cation **6**. Furthermore, it is to be noted that, in the thermal aromatic Claisen rearrangement of prop-2-enyl aryl ethers, the presence of an electron-withdrawing group on the aromatic ring has been shown to retard the rearrangement.[14] If this substituent effect holds for this [3,3]-sigmatropic rearrangement of allenyl(aryl)iodane, the *m*-nitro group of **5** would retard the *ortho* Claisen rearrangement.

Mechanistic alternatives for the preferential formation of **3**, *e.g.* S_N2' reaction, should be considered (Fig. 1) and this process cannot be ruled out.

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