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 BF₃·Et₂O 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 $S_E 2'$ reaction of aryliodanes with propynylsilanes in the presence of BF₃·Et₂O, undergo a reductive iodonio-Claisen rearrangement at -20 °C in dichloromethane yielding orthopropynyliodoarenes 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 products, rearranged 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 mnitroiodobenzene 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 BF₃·Et₂O (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 2aare as follows: in EtOH, 3a (Nu = EtO, 59%) and 2a (33%); in PrOH, 3a (Nu = PrO, 37%) and 2a (32%); in PriOH, 3a(Nu = PriO, 29%) and 2a (62%); in Bu^sOH, 3a (Nu = Bu^sO, 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 mnitroiodane 1 and BF3 Et2O. For instance, reaction of 1 with a large excess of propanol in the presence of BF₃·Et₂O at 30 °C for 4 h gave 1,1-dipropoxypropane in 96% yield. Similar oxidation of BusOH (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^sOH. This BF₃catalysed 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 BF₃. A relatively large primary kinetic deuterium isotope effect $(k_{\rm H}/k_{\rm D} = 4.84)$ observed in the reaction of cyclohexanol- α -[²H] 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, CH_3OH (94), CH_3CH_2OH (93) and (CH₃)₂CHOH (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







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 (RCONH₂) with bis(trifluoroacetoxy)(phenyl)iodane yielding amines (RNH₂) are as follows: R (relative rate), Me (1) < C₅H₁₁ (11) < But (62) < Pri (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 BF₃-catalysed S_E2' reaction of aryliodane 1 with propynylsilane 2 and its follow-up collapse to propynyl cation 6 with reductive elimination of *m*-nitro-

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

Silane 2	Iodane 1 (equiv.)	NuH	t/h	Product 3	
				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 ₉ H ₁₉ OH	24	3a C ₉ H ₁₉ O	(87)
a	2.0	Pr ⁱ OH	2.5	3a PriO	(86)
a	2.0	Bu ^s OH		3a Bu ^s O	(91)
a	2.0	Bu ^t OH	16	3a ButO	(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)
с	1.2	MeOH	2	3c MeO	68(85)
c	1.05	AcOH	2	3c AcO	77(78)
с	1.2	MeCN	3	3c MeCONH	49
d	1.2	MeOH	2	3d MeO	(63)
d	1.05	AcOH	2	3d AcO	56(63)
di	1.2	MeCN	3	3d MeCONH	60

^{*a*} Reactions were carried in the presence of BF₃·Et₂O equivalent to 1 in a nucleophilic solvent (100 equiv.) at room temp. under nitrogen. ^{*b*} Isolated yields. Parenthesis are GC yields.







iodobenzene seems most likely.^{1,10} Similar intermediate propynyl carbocations have been generated by S_N1 solvolysis of allenyl halides in aqueous alcohols.¹¹

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 p 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 mnitrophenyliodonio 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. $S_N 2'$ reaction, should be considered (Fig. 1) and this process cannot be ruled out.

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