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On the Mechanism of Nucleophilic Substitution of Allenyl(aryl)iodine(III): Formation of Propargyl Cation and Competition with Sigmatropic Rearrangement

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Abstract

The ratios of nucleophilic substitution versus [3,3] signatropic rearrangement for the collapse of allenyl(aryl)iodine(III), generated from the reaction of aryliodanes with propargylsilanes in the presence of BF₃-Et₂O in alcohols, were determined. A proposed mechanism involves generation of propargyl cations from the allenyliodine(III) via a unimolecular pathway. © 1998 Elsevier Science Ltd. All rights reserved.

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Allenyl(aryl)iodine(III), generated by S_{F2} ' reaction of propargylsilanes with aryliodanes in the presence of BF3-Et2O, undergoes either reductive iodonio-Claisen rearrangement yielding ortho-propargyliodoarenes [1] or regioselective nucleophilic substitution with nucleophilic solvents, alcohols, carboxylic acids, and nitriles to give propargyl ethers, esters, and amides [2], depending on the electronic nature of the aryliodanes. Reaction of 2-octynylsilane 2b with (diacetoxyiodo)benzene (1c) activated by BF₃-Et₂O in dichloromethane at -20 °C affords exclusively the rearranged ortho-propargyliodobenzene 4 (X = H, $R = n-C_5H_{11}$) in 78% yield, whereas no formation of the rearranged products, 1-(2-iodo-4-nitrophenyl)-2-octyne and 1-(2-iodo-6-nitrophenyl)-2-octyne, was observed in the reaction of **2b** with *m*-nitro-(diacetoxyiodo)benzene (1a) in dichloromethane; this reaction gave *m*-nitroiodobenzene quantitatively, along with the formation of 2-octynyl acetate (6, Nu = OAc, $R = n-C_5H_{11}$; 57%) [2]. The leaving ability of the *m*-nitrophenyliodonio group is evaluated to be 16 times greater than that of the phenyliodonio group [3], and this difference in leaving ability of the aryliodonio groups would determine the reaction course of the intermediate allenyl(aryl)iodine(III) 3, *i.e.*, [3,3] sigmatropic rearrangement and nucleophilic substitution [2]. In the nucleophilic substitutions of allenyl(aryl)iodine(III) 3, both the SN1 mechanism involving generation of propargyl cation 7 and the S_N2' mechanism shown in Scheme 1 are compatible with the regioselective formation of 6. Our results shown here suggest the intermediacy of propargyl cation 7 in this nucleophilic substitution.

Entry	2	1	Product (Yield, %)			_			Product (Yield, %)			
			4 ^b	6 <i>c</i>	(4 : 6) ^{<i>d</i>}	Entry	2	1	4 ^b	5 ^b	6 <i>c</i>	(4+5 : 6) ^d
1	2a	1a	0	57	(0:100)	5	2 b	1a	0	0	86	(0:100)
2	2a	1 b	30	45	(40:60)	6	2 b	1 b	23	0	55	(30:70)
3	2a	1 c	52	19	(73:27)	7	2 b	1 c	45	6	29	(64:36)
4	2a	1 d	60	10	(85:15)	8	2 b	1 d	50	5	18	(75:25)

Table 1	
Substituent Effects on the Reaction of Propargylsilanes 2 with Aryliodanes 1 in Isopropanol	а

a) Reaction conditions: 2 (0.15M)/1 (2 equiv.)/BF3-Et₂O (2 equiv.)/30 °C/2-2.5 h/N₂. b) Isolated yields. c) Determined by GC. d) Ratios of [3,3] sigmatropic rearrangements to nucleophilic substitutions.



Reaction of **2b** with *m*-nitroiodane **1a** in the presence of BF₃-Et₂O in isopropanol exclusively undergoes nucleophilic substitution yielding 2-octynyl isopropyl ether (**6**, Nu = *i*-Pr, R = *n*-C₅H₁₁) in 86% yield (Table 1, Entry 5). We found, however, that the reaction with *p*-chloroiodane **1b** resulted in competition between the nucleophilic substitution and the [3,3] sigmatropic rearrangement, and afforded 2-octynyl isopropyl ether **6** and *ortho*-propargyl-iodobenzene **4** (X = *p*-Cl, R = *n*-C₅H₁₁) in a ratio 70:30 (78%). Furthermore, in the reactions with **1c** and *p*-methyliodane **1d** the formation of a small amount of the conjugated ynone **5**, probably produced via the further oxidation of the rearranged product **4** with **1** at the benzylic position [4], was detected along with **4** and **6**. It is to be noted that the ratios of [3,3] sigmatropic rearrangement (**4+5**) to nucleophilic substitution (**6**) would be highly sensitive to the nature of the substituents; thus, the fraction of rearrangement increases with an increase in the electron-donor ability of the aromatic ring of aryliodanes **1**, *i.e.*, with a decrease in the leaving ability

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Figure 1. Plots of logarithms of the product ratios 6:4+5 in the reactions of 2a (\bigcirc) and 2b (\bigcirc) with 1 (Table 1) vs. logarithms of the rates of solvolysis of 8 in 60:40 (v/v) ethanol-water at 30 °C.



Figure 2. Solvent effects. Plots of logarithms of the product ratios 6:4+5 in the reactions of 2b with 1c vs. Y_{OTS} .

of the aryliodanyl groups [3], in the order $1a \ll 1b < 1c < 1d$ (Table 1, Entries 5-8) [6]. Similar trends of selectivity for sigmatropic rearrangement over nucleophilic substitution were observed in the reaction of unsubstituted propargylsilane 2a (Table 1, Entries 1-4). Most importantly, the substitution to rearrangement ratios observed in the reaction of 1b-d with unsubstituted 2a are always smaller than those with substituted 2b. These results indicate the involvement of generation of propargyl (or allenyl) cation 7 from the allenyliodine(III) 3 via the S_N1 pathway, because the substituted propargyl (or allenyl) cation 7 (R = *n*-C₅H₁₁) must be more stable than the unsubstituted counterpart 7 (R = H) [7]. The alternative S_N2' pathway would expect the decreased substitution to rearrangement ratios on going from 2a to 2b, probably because of the nonbonded interactions between the incoming nucleophile and the R group of 3.

Logarithms of these product ratios of substitution to rearrangement (6:4+5) were found to be correlated linearly with the reported rates of solvolysis of (4-*tert*-butyl-1-cyclohexenyl)aryliodonium salts 8 [3], *i.e.*, the leaving abilities of the aryliodanyl groups, with a correlation coefficient r of 1.00 (Figure 1) [9]. These results reveal that the leaving abilities of the aryliodanyl groups of the allenyl(aryl)iodine(III) 3 play a most important role in determining the reaction course, nucleophilic substitution and [3,3] sigmatropic rearrangement. The slopes are positive and larger than unity (s = 1.43 for 2a and 1.31 for 2b). A slightly larger substituent effect for 2a compared to 2b is compatible with the generation of propargyl cation 7 from the allenyliodine(III) 3 via the S_N1 pathway. Based on Hammond's postulate [10], it is expected that the reaction of 2a generating the less stabilized cation 7 (R = H) exhibits a greater dependence on the nature of the substituents than that of 2b, which generates the more stabilized cation 7 (R = $n-C_5H_{11}$).

The ratios of substitution to rearrangement are also sensitive to the nature of solvents. Solvent effects on the product ratios were measured in the reaction of 2-octynylsilane **2b** with (diacetoxyiodo)benzene **1c** in alcohols in the presence of BF₃-Et₂O at 30 °C. The yields of products **4-6** ($R = n-C_5H_{11}$, X = H) are as follows: in MeOH, **4** (34%) and **6** (Nu = MeO, 32%);

in EtOH, 4 (32%) and 6 (Nu = EtO, 29%); in *i*-PrOH, 4 (45%), 5 (6%), and 6 (Nu = *i*-PrO, 29%); in *t*-BuOH, 4 (48%), 5 (5%), and 6 (Nu = *t*-BuO, 23%). The logarithmic plots of the ratios of substitution to rearrangement (6:4+5) against the solvent ionizing power Y_{OTs} [11] (Figure 2) and Y^+ [12] were correlated linearly with slopes m = 0.13 (r = 0.98) and m = 0.99 (r = 0.98), respectively [13,14]. A small positive slope (m = 0.12) against Y_{OTs} was reported for SN1 solvolysis of (4-*tert*-butyl-1-cyclohexenyl)aryliodonium ions 8, which involves formation of a vinyl cation from the ionic substrate [3]. These m values suggest that the intermediate, which generates propargyl cation 7 via SN1 solvolysis in alcohols, would be allenyl(aryl)-iodonium ion 9 rather than the hypervalent allenyl(aryl)iodanes.



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