JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 11
1990

Amination Reaction of Allylic Chlorides with Silver Iodide/Lithium *N,N*-Disilylamide Mixed Reagents

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The nucleophilic substitution of allylic chlorides with silver iodide/lithium *N,N*-disilylamide mixed reagents gives protected primary allylic amines in good to excellent yields.

Alkali metal *N,N*-disilylamides have been used as hindered strong bases in organic synthesis for more than twenty years.[1,2] However, only a few examples of their application as nitrogen nucleophiles have been reported owing to their poor nucleophilicity.[3—5] Furthermore, when the substrate has more acidic protons, hydrogen abstraction predominates nucleophilic substitution.[5]

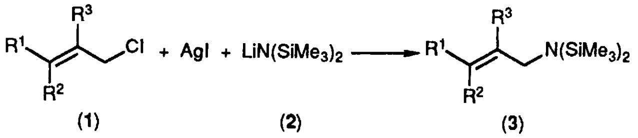
We have now found that silver iodide (AgI)/lithium *N,N*-bis(trimethylsilyl)amide (**2**) mixed reagents nucleophilically attack allylic chlorides to give primary allylic amines protected with a silyl group.[6,7]

N,N-Disilylamination was generally carried out by stirring allylic chlorides with AgI and (**2**) under reflux in tetrahydrofuran (THF) (Scheme 1). AgI is generally highly insoluble, but in this case it dissolved completely in THF containing (**2**). Brown solids gradually precipitated as the reaction proceeded. As shown in Table 1, the nucleophilicity of (**2**) was greatly enhanced by mixing not more than 0.5 equiv. of AgI with (**2**), and *N,N*-disilylamines were obtained in high yields from (**1a**—**e**). Although a similar effect was observed using NaI and CuI, the reaction required a longer reaction time or gave the products in lower yields. It is noteworthy that 1 equiv. of AgI was not effective in these cases. On the other hand, *N,N*-disilylamination of (**1f**) was attained only by using 1 equiv. of AgI/(**2**). When a catalytic amount of AgI or a stoicheiometric amount of NaI or CuI was used for (**1f**), 1,6-diphenylhexa-1,3,5-triene was obtained as a major product, which may be formed *via* hydrogen abstraction at the carbon substituted with Cl. For (**1e**) the Cl on the vinylic carbon was inert under the reaction conditions and did not affect the reaction course. The reaction of 1-chloroallylsilane (**1g**)[8] with 1 equiv. of AgI/(**2**) proceeded highly regio- and

Table 1. Substitution reaction of allylic chlorides with silver iodide/lithium *N,N*-disilylamide mixed reagents.[a]

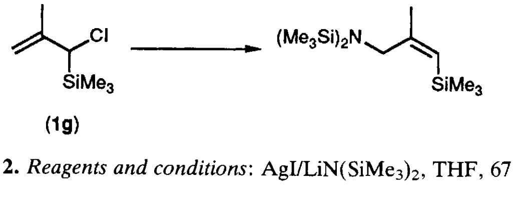
	Ratio of AgI: (**1**)	*t*/h	Yield of amine (**3**)/%
(**1a**)	0	20	0[b]
	0.5	48	72[b]
(**1b**)	0	20	25
	0.1	1.5	99
	0.5	1.5	100
	0.75	1.5	22
(**1c**)	0	20	Trace
	0.1	6	54[c]
(**1d**)	0	20	5[b]
	0.1	6	78[b]
(**1e**)	0	20	6
	0.1	3	60
(**1f**)	0.1	20	1
	1	20	59

[a] Molar ratio, chlorides: $LiN(SiMe_3)_2$ = 1:1.2. Unless otherwise noted, reactions were run at reflux temperature in THF. [b] Reaction run at room temperature. [c] Two equivalents of $LiN(SiMe_3)_2$ were used.



a; $R^1 = R^2 = R^3 = H$
b; $R^1 = Me, R^2 = R^3 = H$
c; $R^1 = R^2 = H, R^3 = Me$
d; $R^1 = R^2 = Me, R^3 = H$
e; $R^1 = Me, R^2 = Cl, R^3 = H$
f; $R^1 = Ph, R^2 = R^3 = H$

Scheme 1



(**1g**)

Scheme 2. *Reagents and conditions*: AgI/$LiN(SiMe_3)_2$, THF, 67 °C.

stereo-selectively in S_N2' manner to give (*Z*)-1-[bis(trimethylsilyl)amino]-(2-methyl)vinyltrimethylsilane in 54% yield (Scheme 2).

The present reaction is still mechanistically ambiguous. Although it is possible that the process occurs *via* iodination of allylic chlorides, it is not understood why a stoicheiometric amount of AgI was not effective in many cases or why the reaction of allyl iodide with (**2**) was also facilitated by adding a catalytic amount of AgI. Furthermore, *ca.* 60% of AgI can be recovered from the reaction mixture and reused for the amination reaction with the same degree of efficiency as before.

Further application of the AgI/(**2**) mixed reagents and mechanistic details will be reported in due course.

Received, 26th February 1990; Com. 0/00861C

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