



Strontium-Mediated Selective Protonation of Unsaturated Linkage of Aromatic Hydrocarbons and These Derivatives

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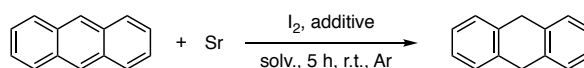
ABSTRACT

The selective protonation of aromatic hydrocarbons with at least two or more aromatic rings and aromatic compounds bearing unsaturated linkages can be achieved by metallic strontium metal with ammonium chloride and iodine, or ammonium iodide in tetrahydrofuran. The reaction system is ammonia-free in room temperature and the reaction proceeds high selectivity in moderate to good yields.

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The reduction of aromatic hydrocarbons by alkali metals in liquid ammonia is a powerful and versatile method. Classical Birch reductions of aromatic hydrocarbons are performed with alkali metals in liquid ammonia at below $-33\text{ }^{\circ}\text{C}$, or reflux temperature of alcohols in the presence of ammonia.¹ These reactions can be tuned by varying conditions, temperatures, metals, additives, proton sources or quenching reagents.² A cathodic Birch reduction has been reported for a limited class of substrates.³ Recently, several ammonia-free reductions of aromatic rings under ambient or higher temperature were reported. For example, hydrogenation of polycyclic hydrocarbons was promoted by transition metal complexes⁴ or nanoparticles⁵ under hydrogen gas, alkali metals on silica gel,⁶ samarium(II) iodide,⁷ frustrated Lewis pair⁸ and hydroxide ion was used as an electron source for photochemistry activated Birch reduction of naphthalene derivatives.⁹ We have been investigating synthetic reactions using organostrontium compounds and have reported that the dialkylation of esters with alkyl iodides or esterification of bulky alcohols with strontium compounds proceeds smoothly using metallic strontium to afford the corresponding adducts in good yields.¹⁰ Recently, we found that aromatic hydrocarbons with at least two or more aromatic rings and aromatic compounds bearing unsaturated linkages reacted with metallic strontium to give partially protonated corresponding compounds in moderate to good yields. Herein, we demonstrate partial protonation of several aromatic hydrocarbons and these derivatives using metallic strontium with ammonium salts and iodine sources at room temperature.

Table 1
Protonation of anthracene with Sr-mediated condition.



entry	Sr (eq.)	solv.	I ₂ (mol%)	additive (eq.)	yield (%)
1	1.0	THF	-	-	-
2	1.1	THF	10	-	10
3	1.1	THF	10	NH ₄ Cl (5.0)	37
4	1.1	THF	10	NH ₄ Cl (10)	50
5	1.7	THF	15	NH ₄ Cl (10) ^a	79
6	1.2	THF	15	urea (10) ^a	trace
7	1.5	THF	15	NH ₄ NO ₃ (10) ^a	9
8	1.5	THF	15	(NH ₄) ₂ SO ₄ (10) ^a	8
9	2.5	THF	15	NH ₄ Cl (10) ^a	99
10	2.5	Et ₂ O	15	NH ₄ Cl (10) ^a	trace
11	2.5	MeCN	20	NH ₄ Cl (10) ^a	5
12	2.5	MeOH	15	NH ₄ Cl (10) ^a	8
13	2.5	2-PrOH	20	NH ₄ Cl (10) ^a	-

^a Dried under vacuum with heat before operation.

The selective protonation of anthracene with strontium metal was investigated (Table 1). This reaction was proceeded at ambient temperature to afford 9,10-dihydroanthracene in the presence of 1.1 eq. strontium under argon (Table 1, entry 3). The results of control experiments showed the Sr-mediated protonation reaction required iodine source¹¹ and ammonium chloride (Table 1, entries 1 and 2). An increase in the amount of ammonium chloride resulted in an increase in yield (Table 1, entry 4). Other ammonium salts or urea, or using other common solvents had no impact on the reactivity (Table 1, entries 6, 7, 8 and 10-13). Finally, we found that pre-dried ammonium chloride activated the reaction condition (Table 1, entry 5), with 2.5 equiv. of metallic strontium and 15 mol% of iodine providing the best results in terms of reaction efficiency (Table 1, entry 9).

The reduction of aromatic hydrocarbons with other alkali metal or alkaline-earth metal under pre-dried ammonium chloride with iodine conditions were also investigated by using anthracene as a model compound (Table 2). From the results, lithium, sodium, magnesium and barium showed less activation of the protonation reaction (Table 2, entries 1, 2, 4 and 6). On the other hand, potassium and calcium gave good yields of 1,9-dihydroanthracene (Table 2, entries 3 and 5). Although these results suggested that the reduction system might be able to be also carried out with potassium or calcium instead of strontium, these metals usually have a problem for the reaction protocol compared with using strontium metal.¹²

Table 3 shows the scope of the selective protonation reaction. In the cases of substrates composed at least two or more polycyclic



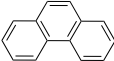
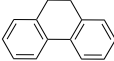
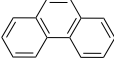
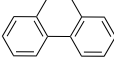
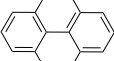
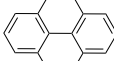






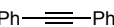


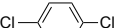
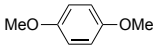
benzene rings, the reaction gave the corresponding selective protonated compounds in moderate to good yields (Table 3, entries 1, 2 and 4). It is noteworthy that 9,10-dihydrogenated phenanthrene was obtained in better yield of 77 % by using 2-propanol as a solvent (Table 3, entry 3). Aromatic compounds bearing unsaturated linkages were protonated and obtained in moderate to good yields, respectively (Table 3, entries 5-8). In sharp contrast, the reductions of biphenyl, *p*-dichlorobenzene and *p*-dimethoxybenzene would not progress the protonation and recovered starting materials (Table 3, entries 9-11).

Table 2
Protonation of anthracene with alkali / alkaline-earth metals, iodine and ammonium chloride.

entry	Metal (eq.)	time (h)	yield (%)
1	Li (3.0)	5	20
2	Na (3.0)	5	13
3	K (3.0)	5	90
4	Mg (3.0)	10	-
5	Ca (3.0)	10	80
6	Ba (3.0)	10	trace

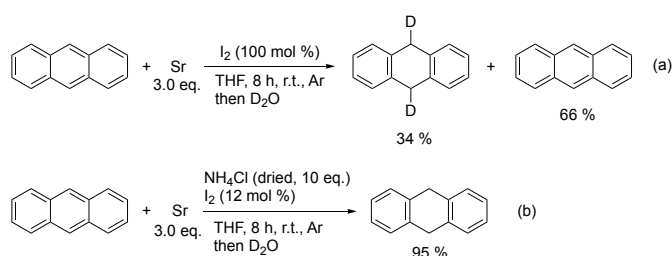
Table 3

Protonation of aromatic hydrocarbons and aromatic compounds bearing unsaturated linkage under strontium condition.

entry	substrate	Sr (eq.)	I ₂ (mol%)	time (h)	product	yield (%)
1		3.9	25	12		81
2		3.9	50	12		57
3		4.0	30	7		77 ^[a]
4		3.3	20	3		65
5		3.5	40	10		93
6		3.5	10	10		81
7		3.5	10	10		70
8		3.5	40	10		82
9		3.2	40	12	no reaction	-
10		2.8	40	12	no reaction	-
11		3.3	40	12	no reaction	-

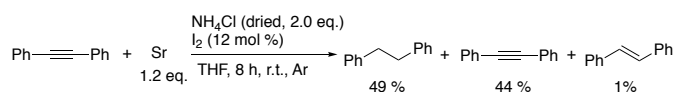
^a 2-PrOH was used as a solvent.

From these results, it is supposed to be required for ammonium ion and iodide ion in the hydrogenation reactions. In our previous works, metallic strontium is activated by iodine, selectively.^{10,11} To investigate the role of ammonium ion, we have carried out the experiment of reduction of anthracene without ammonium chloride. The reaction was progressed in the presence of 100 mol% of iodine, and then quenched by deuterium oxide (Scheme 1a). The reduced anthracene was obtained with over 99 % deuterium incorporated, although the yield was less than that of under ammonium salt condition. Compared with the reaction in the presence of ammonium chloride and quenched by deuterium oxide, the obtained compound was only protonated 1,9-dihydroanthracene (Scheme 1b). Thereby, ammonium ion might be work as a proton source and stabilizer for the sensitive intermediate species which are interacted with strontium species.



Scheme 1. Investigation of deuterium incorporation in the reduction of anthracene with strontium metal and iodine (a) or iodine/ammonium salt (b) conditions.

On the other hand, we tried to obtain stilbene, which is semi-protonated compound of diphenylacetylene by stoichiometric control of metallic strontium. However, about 50 % yield of full-protonated 1,2-diphenylethane was obtained and only 1 % of stilbene was observed (Scheme 2). The result was also supported that the electron transfer from metallic strontium to some of substrates occurs through interactions between metal to π -system.^{7a,b}



Scheme 2. Protonation of diphenylacetylene with the same equivalent of strontium metal condition.

Furthermore, we also found that ammonium iodide worked as an activator and proton source in the protonation reaction. The reaction with 3 equivalent of pre-dried ammonium iodide and metallic strontium in tetrahydrofuran afforded the corresponding protonated aromatic hydrocarbons and these derivatives (Table 4). These yields were similar to the case of using ammonium chloride with iodine condition (Table 4, entries 1, 2, 3 and 5-9). It is noteworthy that better yield of 9,10-dihydrogenated phenanthrene was also obtained used by 2-propanol as a solvent (Table 4, entry 4).

In summary, we found that metallic strontium with ammonium salt and iodine source conditions could be used as reductant in protonation of aromatic hydrocarbons or unsaturated linkage of these derivatives under liquid ammonia-free condition. Compared to the conventional Birch reduction, the method could offer some advantages in terms of environmental, equipment and safety

standpoints. The investigation of the limitation, other application and detail of the reaction mechanism is now in progress.

Table 4
Strontium-mediated selective protonation with ammonium iodide.

substrate + Sr		NH ₄ I (dried, 3 eq.)		Protonated substrate	
		THF, time r.t., Ar			
entry	substrate	Sr (eq.)	time (h)	yield (%)	
1		1.3	6	98	
2		1.6	6	78	
3		2.0	10	31	
4		2.0	10	49 ^[a]	
5		3.5	8	47	
6		1.7	6	91	
7		1.7	6	79	
8		1.7	6	70	
9		1.2	10	96	

^a 2-PrOH was used as a solvent.

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11. Iodine is used as an activator for metallic strontium. Although catalytic amount of methyl iodide is also able to activate the reaction, a trace amount of methylated compound is observed.
12. In the case of using potassium metal in the protonation reaction, a fire was often lit when the reaction was quenched. On the other hand, not starting materials but undesired byproducts were obtained with protonated products when calcium metal was used in the reaction.

Supplementary data

Supplementary data (general information, synthesis, procedure, and spectral data) associated with this article can be found, in the online version, at doi: 10.1016/xxxxxxxxxxxxxx.