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TETRAHEDRON

Tetrahedron 56 (2000) 9927–9935

Generation and Reactions of Alkynylsamariums

Munetaka Kunishima,* Daisuke Nakata, Shinobu Tanaka, Kazuhito Hioki and Shohei Tani

Faculty of Pharmaceutical Sciences, Kobe Gakuin University, Nishi-ku, Kobe 651-2180, Japan

Received 28 August 2000; accepted 17 October 2000

Abstract—Three methods have been developed for generating alkynylsamariums: (1) reduction of iodoalkynes with SmI_2 in the presence of HMPA, (2) deprotonation at the terminal position of 1-alkynes either by tetrahydrofurylsamarium generated by PhI and SmI_2 in THF, or, (3) deprotonation by butyllithium followed by metal–metal exchange with SmI_3. Alkynylsamariums arising from iodoalkynes with SmI_2 undergo coupling with carbonyl compounds under both Barbier and Grignard conditions in benzene-HMPA or THF-HMPA as a solvent system. Tetrahydrofurylsamarium generated from iodobenzene and SmI_2 in THF can deprotonate from terminal alkynes to yield alkynylsamariums whereas other alkylsamariums, such as ethyl-, isopropyl-, cyclohexyl-, and cyclopentylsamarium do not work well. Metal–metal exchange between an alkynyllithium and SmI_3 is also effective; the reactive species in this case would be alkynylsamariums rather than alkynyllithiums. To reveal the properties of alkynylsamariums, we examined the stability and reactivity of alkynylsamariums toward various electrophiles.

Introduction

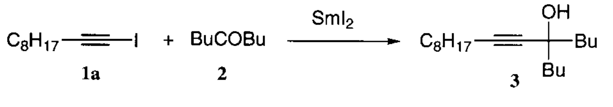
In the past decade, many types of reactions involving organosamariums have been developed.[1–7] The most useful and common reactions of organosamariums for carbon–carbon bond formation are the samarium Barbier reaction (SBR) and the samarium Grignard reaction (SGR).[8] The principal advantages of SBR and SGR in comparison with conventional reactions of magnesium or lithium lie in their ability to effect rapid, mild and chemoselective reduction of organohalides. Both inter- and intramolecular versions of these reactions using primary and secondary alkyl halides have been well established. Combining SGR or SBR with other anionic or radical processes induced by SmI_2 enables the construction of complex molecules in a one-pot reaction (sequential reaction).[5,6] Curran and Totleben studied the generation, reactivity and stability of alkylsamariums extensively.[3c] In particular, they examined the reactions of alkylsamariums with several kinds of electrophiles. In contrast to these thorough studies on alkylsamarium, reactions involving aryl-, vinyl-, or alkynylsamariums are very limited. Because aryl or vinyl radicals abstract a hydrogen from THF when it is used as a solvent faster than they are reduced by SmI_2,[9] these reactive radicals resulting from a single electron transfer (SET) from SmI_2 to aryl or vinyl halides are difficult to transform into the corresponding organosamariums.[10] We were able to overcome this difficulty by using a benzene-HMPA system, in which the coupling of aryl or vinyl halides with carbonyl compounds successfully proceeded.[11] Recently, we reported coupling reactions of alkynyl iodides with carbonyl compounds via alkynylsamariums.[12] We now report our further studies on the generation and the reactivity of alkynylsamariums.

Results and Discussion

Reduction of organohalides with SmI_2 is probably the most common method for generating organosamariums. Thus we have chiefly employed the reaction of 1-iodoalkynes with SmI_2 to generate alkynylsamariums. More direct methods of generating alkynylsamariums that avoid the preparation of 1-iodoalkynes from 1-alkynes would be both useful and practical. For this reason, we explored other methods involving deprotonation of 1-alkynes at the terminal sp-carbon by an organosamarium or by a base, like butyllithium followed by metal–metal exchange.

SBR and SGR of 1-iodoalkynes

Reaction of iododecyne (**1a**, 1.0 equiv.) and dibutyl ketone (**2**, 1.5 equiv.) with SmI_2 (4 equiv.) carried out by the SBR



Run	Method	Solvent	**1a** / **2** / SmI_2	Yield
1	SBR	benzene	1 : 1.5 : 4	78%
2	SGR	benzene	1 : 1.5 : 4	70%
3	SBR	THF	1 : 1.5 : 10	84%
4	SGR	THF	1 : 1.5 : 2.5	61%

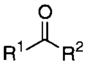
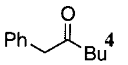
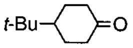
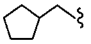
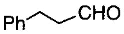
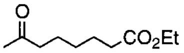
Scheme 1.

Keywords: samarium and compounds; Grignard reactions/reagents; alkynes; alkynyl halides.

* Corresponding author. Tel.: +81-78-974-1551; fax: +81-78-974-5689; e-mail: kunisima@kgu-p.pharm.kobegakuin.ac.jp

PII: S0040-4020(00)00971-6

Table 1. Samarium Barbier reactions of 1-iodoalkynes in benzene

Run	R of iodoalkynes R—≡—I		Yield of alkyne adduct (%)[a]
1	**1a**	 **4**	76
2	**1a**	 **5**	76[b]
3	**1b** Ph	**2**	75
4	**1c** 	**2**	78
5	**1a**	EtCHO **6**	58
6	**1a**	 **7**	65
7	**1a**	 **8**	67

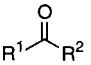
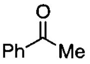
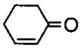
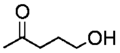
[a] Isolated yield. **1**:ketone or aldehyde:SmI_2=1.0:1.5:4.0.

[b] A mixture (84:16) of axial/equatorial alcohols, whose stereochemistry is not determined.

method in benzene-HMPA (9:1) afforded 5-butylpentadec-6-yn-5-ol (**3**) in 78% yield, as illustrated in Scheme 1, Run 1.[13] Similarly, both aliphatic ketones (**2**, **4**, **5**) and aldehydes (**6**, **7**) gave the corresponding propargyl alcohols in fairly good yields (see Table 1). In the case of a keto ester (**8**), alkynylation took place chemoselectively at the ketone. Alkynylation was found to proceed under SGR conditions (Scheme 1, Run 2). Thus treatment of **1a** with SmI_2 in benzene-HMPA for 10 min, followed by sparging with dry air in an effort to decompose excess SmI_2 with oxygen prior to addition of **2**, afforded **3** in 70% yield.[14]

In contrast to alkenyl and arylsamariums, which generally do not form in THF,[9] alkynylsamariums can be generated in THF and undergo coupling with ketones in good yield, using either the Barbier or the Grignard method (Scheme 1, Run 3, 4). The SBR reaction of **1a** and **2** with a large excess amount of SmI_2 performed in THF-HMPA (9:1) gave the alcohol (**3**) in 84% yield, and no THF-adduct (**12**) was detected. When the reaction mixture of **1a** and SmI_2 was quenched with D_2O instead of the addition of ketone (**2**), incorporation of 60% deuterium atom at the terminal sp-carbon of 1-decyne (65% yield) was observed (Eq. (1)). No significant difference between benzene and THF was observed; however, the SGR procedure seems to produce better results than the SBR procedure. As shown in Table 2, both aromatic ketone (**9**) and α,β-unsaturated ketone (**10**), which were found to be unsuitable for the SBR conditions presumably because of their high reactivity toward SmI_2, were allowed to couple with iodoalkyne under the SGR conditions.[15] Under SGR conditions, coupling of alkynylsamariums (**13a**) with a hydroxyketone (**11**) occurs more quickly than protonation by the hydroxy group.

Table 2. Samarium-mediated coupling reactions of 1-iodododecyne (**1a**) and carbonyl compounds

	Yield of alkyne adduct (%)[a]		
	SBR[b] in benzene	SGR[c] in benzene	SGR[d] in THF
 **9**	0[d]	64	92
 **10**	0[d]	46	55
 **11**	0[d]	46[e]	46

[a] Isolated yield.

[b] **1a**:ketone or aldehyde:SmI_2=1.0:1.5:4.0.

[c] **1a**:ketone or aldehyde:SmI_2=1.0:1.5:2.5.

[d] A complex mixture composed of many products was obtained.

[e] **1a**:ketone or aldehyde:SmI_2=2.0:1.0:5.0.

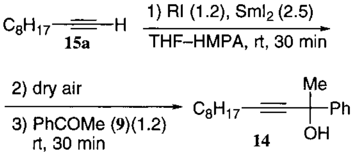
$$\mathbf{1a}\ \xrightarrow[\text{2) Dry Air}]{\text{1) SmI}_2\text{ (excess) THF–HMPA rt.10min}}\ \Big[\underset{\mathbf{13a}}{C_8H_{17}{-}{\equiv}{-}SmI_2}\Big]\ \xrightarrow{D_2O}\ \underset{\text{y. 65 \% (60\% D)}}{C_8H_{17}{-}{\equiv}{-}D} \qquad (1)$$

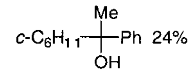
These findings clearly indicate that alkynylsamariums act as an intermediate in both benzene-HMPA and THF-HMPA. To examine the stability of alkynylsamariums, we added acetophenone (**9**) at defined times to a stirred reaction mixture of **1a** and SmI_2. Yields of the alkyne adduct (**14**) as a function of the reaction time indicate the half-life period of decynylsamarium in THF to be 5 h at 25°C.

Generation of alkynylsamariums from terminal alkynes

Because the terminal C–H bonds of alkynes are more acidic than the C–H bonds of alkanes, we assumed that deprotonation of alkynes by alkylsamariums could afford alkynylsamariums. A mixture of an alkyl iodide and 1-decyne (**15a**) in THF was treated with SmI_2 for 30 min followed by addition of **9**. As summarized in Table 3, Runs 1–5, this process was unsuccessful when primary, secondary and tertiary iodides were used. In contrast to the results obtained with alkyl iodides, 49% yield of the alkynyl adduct (**14**) was obtained by using iodobenzene. The yield of **14** was improved to 81% by increasing the amounts of reagents [iodobenzene (3 equiv.), SmI_2 (6 equiv.) and acetophenone (3 equiv.)]. To further examine the reaction pathway, we carried out additional experiments, as illustrated in Eqs. (2) and (3). Treatment of iodobenzene and **15a** with SmI_2 in the presence of dibutyl ketone gave the THF adduct (**12**) in 41% yield without the formation of the alkyne adduct. Iodobenzene with SmI_2 in THF is known to generate tetrahydrofurylsamarium (**16**) as a result of a hydrogen atom abstraction from THF by a phenyl radical.[9] Tetrahydrofurylsamarium (**16**), probably formed in the same way, underwent coupling with ketone faster than deprotonation from **15a** in the presence of ketones.[16] In the absence of

Table 3. Attempt to generate decynylsamarium by deprotonation with alkylsamariums



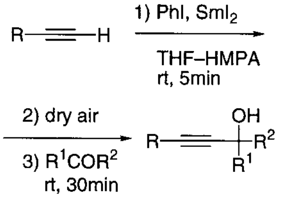
Run	RI	Yield	
1	EtI	0%	
2	*i*-PrI	12%	
3[a]	*c*-$C_6H_{11}I$	0%	 $c\text{-}C_6H_{11}C(Me)(OH)Ph$ 24%
4	*c*-C_5H_9I	18%	
5	*t*-BuI	trace	
6	PhI	49%	
7[b]	PhI	81%	
8[c]	PhI	trace	

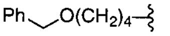
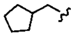
[a] The ratio of decyne:RI:**9**:SmI_2 is 1:1.5:1.5:3.

[b] The ratio of decyne:RI:**9**:SmI_2 is 1:3:3:6.

[c] Performed in THP in place of THF.

Table 4. Grignard-type coupling of alkynylsamariums generated by the mediation of iodobenzene

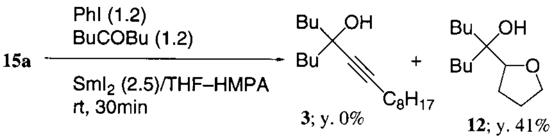


R	R^1COR^2	Yield[a] (%)
	**9**	76
Ph-	**9**	60
Me_3Si-	**9**	40
	**9**	72
C_8H_{17}–	**2**	56
C_8H_{17}–	Ac_2O	43[b]

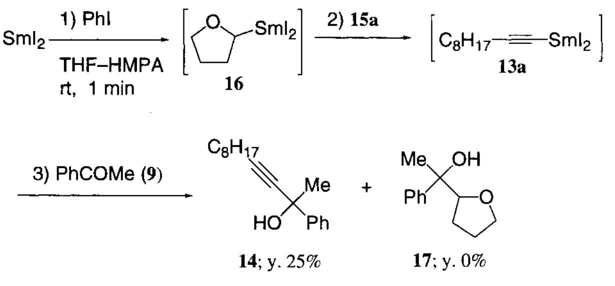
[a] The corresponding propargyl alcohols were formed.

[b] Decynyl methyl ketone was obtained.

ketones, the deprotonation proceeded to give decynylsamarium. In fact, stepwise addition of the reactants to a solution of SmI_2 in the order of iodobenzene, **15a**, and **9** yielded **14** (25%) as a major product; no THF adduct (**17**) was observed (Eq. (3)). Interestingly, the reaction performed in THP in place of THF gave only a trace of **14** along with starting materials (Table 3, Run 8). The poor result in THP also indicates the mediation of THF.



(2)

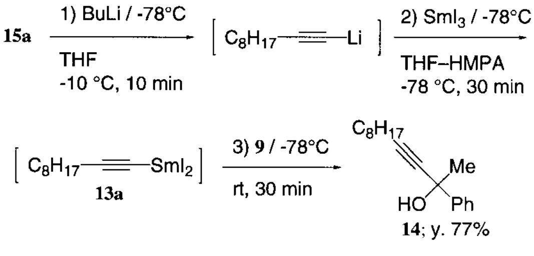


(3)

The result with *t*-butyl iodide (Table 3, Run 5), in which neither the *t*-butyl adduct nor the decynyl adduct was formed, is in good agreement with the fact that tertiary alkyl iodides are not converted into alkylsamariums by SmI_2.[3c] Curran and Totleben reported that ethyl and isopropyl iodide underwent SBR in fair to good yield whereas no coupling occurred by SGR because of their instability under the SGR conditions.[3c] Their results indicate that ethyl- and isopropylsamarium can be generated from the corresponding halides with SmI_2 but are too unstable to undergo coupling with ketones under SGR conditions. Therefore, the poor results with ethyl and isopropyl iodide (Runs 1, 2) can be attributed to the decomposition of the alkylsamarium intermediates before deprotonation from 1-alkynes. Actually, neither the ethyl nor isopropyl adduct was detected as a by-product in either conditions.

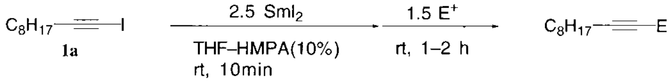
We attempted the reaction using cyclohexyl iodide because the compound is known to undergo both SBR and SGR reaction in good yields.[3c] Surprisingly, no decynyl adduct was formed along with the 24% yield of the cyclohexyl adduct. As described above, decynylsamarium should be stable during the reaction and give its adduct in a reasonable yield; therefore, proton transfer from **15a** to cyclohexylsamarium would be quite slow. It is not clear why only **16** deprotonates effectively from **15a** while other alkylsamariums do not. It is possible that the etheral oxygen of THF participates in or promotes the deprotonation step. The generation of **14**, albeit in a low yield (18%), when cyclopentyl iodide was used may indicate that five-membered cycloalkylsamariums are more liable to deprotonation. The poor yield observed in THP may support the latter supposition. Otherwise, the unsuccessful result in THP can be attributed to decreasing the rate of a hydrogen atom abstraction of phenyl radical from THP.[6a] Some examples for SGR using the iodobenzene-alkyne-SmI_2 system are shown in Table 4. Phenyl- and trimethylsilylacetylene as well as aliphatic alkynes were available.

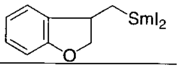
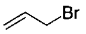
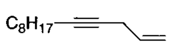
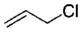
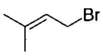
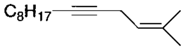
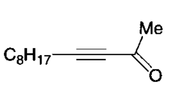
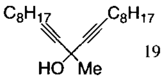
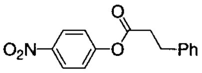
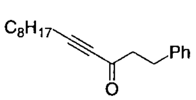
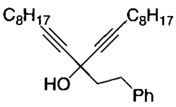
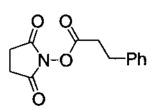
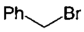
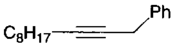
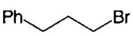
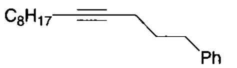
An alternative method of generating alkynylsamariums by deprotonation is via a metal–samarium exchange.[17,18] To examine this possibility, we treated 1-decynyllithium with SmI_3, generated from Sm and I_2, at −78°C for 0.5 h. The mixture was then treated with **9** to give **14** in 77% yield (Eq. (4)). The actual reactive species adding to the ketone can be considered decynylsamarium (**13a**) rather than decynyllithium, as discussed in the next section.



(4)

Table 5. Attempt to trap decynylsamarium with various electrophiles



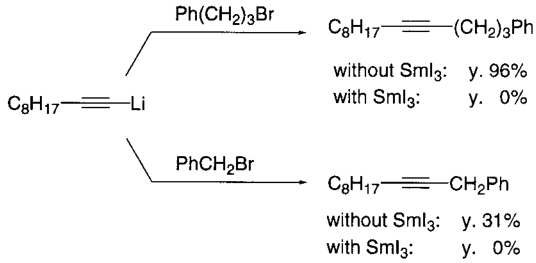
Run	EX	Product				Reaction with Alkylsamarium[a] 
1			71%			unsuccessful
2			41%			unsuccessful
3			88%			39%[d]
4	TMSCl	$C_8H_{17}C{\equiv}C{-}TMS$	71%			unsuccessful[e]
5[b]	Ac_2O		72%		19%	55%[f,g]
6	AcCl		0%		0%	unsuccessful[h]
7	PhSSPh	$C_8H_{17}C{\equiv}C{-}SPh$	0%			65%[g]
8			<3%		43%	NC[i]
9			<3%		12%	NC[i]
10			0%			unsuccessful
11[c]			0%			NC[i]

[a] Reported by Curran and Totleben; Ref. 3c. The 'unsuccessful' indicates that either poor yields of product or no product was obtained.
[b] **1a**:SmI_2:E^+=1:2:1.
[c] **1a**:SmI_2:E^+=1:2.5:1.5.
[d] A 2/1 mixture of S_N2'/S_N2 regioisomers.
[e] Silylation of perfluoroalkylsamarium was reported to be successful: Ref. 17.
[f] The result using $(i\text{-}PrO)_2O$ as an acid anhydride.
[g] Molander and McKie also reported: Ref. 3d.
[h] The result using PhCOCl as an acid chloride.
[i] NC: not conducted.

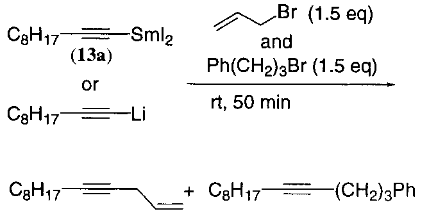
Coupling reaction of alkynylsamariums with electrophiles

To survey the chemical property of alkynylsamariums, we explored reactions of decynylsamarium with several kinds of electrophiles. 1-Iododecyne was treated with SmI_2 for 1–10 min followed by addition of an electrophile, and the reaction mixture was stirred for 1–2 h. Results are summarized in Table 5 along with those of alkylsamariums reported by Curran and Totleben for comparison.[3c] As is evident, the reactivity of alkynylsamariums is considerably different from that of alkylsamariums. The ^1H NMR spectra of the crude products indicated that the common by-product was 1-decyne along with unreacted starting material 1-iododecyne in every case. Allyl bromide, which was reported to afford a trace amount of coupling product with alkylsamarium, was found to couple with 1-decynylsamarium in 71% yield. Prenyl bromide reacted with 1-decynylsamarium selectively at the allylic position (S_N2 process) in 88% yield whereas an alkylsamarium was shown to react in a moderate yield with a low S_N2/S_N2' selectivity. TMSCl, which does not couple with an alkylsamarium, underwent coupling with **13a** in 71%.[18b,19] By contrast, diphenyldisulfide, which reacts with an alkylsamarium, did not react with 1-decynylsamarium. An acid anhydride was found to successfully react to give the corresponding alkynyl ketone along with the bisdecynylated tertiary alcohol whereas an acid chloride yielded neither the ketone nor the alcohol. The reactivity of alkynylsamariums toward an acid anhydride and an acid chloride is similar to that of alkylsamariums.[3c,d] Reaction with the activated ester derived from 3-phenylpropionic acid and 4-nitrophenol or *N*-hydroxysuccinimide resulted in the formation of bisdecynylated alcohol. The reaction with 3-phenylpropyl bromide or benzyl bromide was unsuccessful, giving the corresponding alkyl iodides that were probably formed by halogen-exchange. Although reductive coupling of benzyl bromide giving 1,2-diphenylethane was reported in the case of an alkylsamarium,[3c] no such product was obtained with alkynylsamariums under the conditions we employed.

Alkynylsamariums generated from iodoalkynes and SmI_2 coupled with ketone in good yield under SGR conditions and did not couple with 3-phenylpropyl or benzyl bromide (see Table 5, Run 10, 11). On the other hand, decynyllithium underwent coupling with these alkyl bromides (Eq. (5)). When decynyllithium was treated with SmI_3 followed by addition of these alkyl bromides, no coupling product was formed (Eq. (5)). These results indicate that the reactivity of decynyl anion generated from lithium–samarium exchange is more similar to that of decynylsamarium generated from 1-iododecyne than that of decynyllithium. The observed reactivity of alkynylsamariums toward electrophiles is useful for chemoselective alkynylation. For example, when decynylsamarium **13a** generated from **1a** under SGR conditions was treated with a mixture of allyl bromide (1.5 equiv.) and 3-phenylpropyl bromide (1.5 equiv.), tridec-1-en-4-yne was selectively produced in 79% yield with no detectable amount of 1-phenyl-4-tridecyne, whereas the reaction using decynyllithium under similar conditions gave the both coupling compounds (Eq. (6)). For another example, in contrast to the chemoselective reaction of decynylsamarium with keto ester of **8** (Table 1, run 7), a reaction of decynyllithium with **8** resulted in the formation of a complex mixture of unidentified products.



(5)

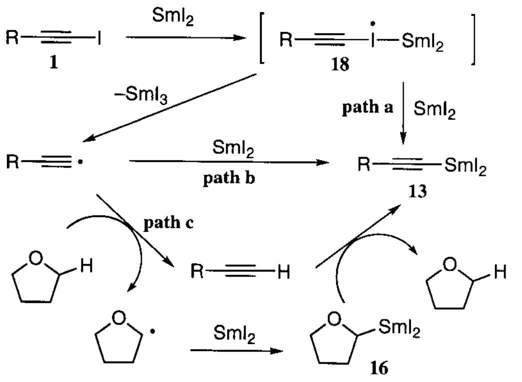


(6)

from	yield	yield
13a	79%	0%
decynyllithium	34%	9%

Mechanistic considerations in the generation of alkynylsamariums from iodoalkynes

It is reasonable to assume that the alkynylsamariums would be generated by successive single electron transfers from SmI_2 to alkynyl iodides via alkynyl radicals in benzene-HMPA (Scheme 2, path b).[20] In the case of THF-HMPA, however, a similar mechanism leading to the formation of alkynylsamariums seems to be unlikely, if alkynyl radicals, which are a very energetic species and therefore very reactive toward THF, are involved.[21] A more likely explanation for the generation of alkynylsamariums in THF is shown in path c. An initially formed alkynyl radical would abstract a hydrogen atom from THF to afford an alkyne and tetrahydrofuryl radical. The radical would then be reduced by SmI_2 to its anion (**16**), which undergoes deprotonation from the alkyne to lead to the corresponding alkynylsamarium. Evidence supporting the possibility of this mechanism involving deprotonation by **16** was provided by the reactions using iodobenzene and 1-decyne, as described in Eq. (3) and Tables 3 and 4. However, the reaction of iodobenzene and 1-decyne with SmI_2 in the presence of a ketone gave the THF adduct only (Eq. (2)) whereas SBR of iodoalkynes with ketones in THF afforded the alkyne adduct only without THF adduct. This inconsistency indicates the possibility that another mechanism is involved, one that does not generate the alkynyl radicals shown in path a. Since alkynyl radicals are very unstable,[21] a radical (**18**) resulting from complexation of SmI_2 and iodoalkyne (**1**) could receive the second electron from another SmI_2 faster than elimination of SmI_3 giving an alkynyl radical.[22]



Scheme 2.

Conclusion

In this paper, we have described the generation, stability, and reactivity of alkynylsamariums. As noted, three methods are available for generating alkynylsamariums: (1) reduction of alkynyl halides with SmI_2 in THF or benzene in the presence of HMPA, (2) deprotonation at the terminal position of 1-alkynes by tetrahydrofurylsamarium generated by iodobenzene and SmI_2 in THF, (3) metal–metal exchange between alkynyllithium and SmI_3.

Reaction of alkynyl halides with ketones or aldehydes took place under SGR conditions as well as SBR conditions. The scope of SGR is broader than the SBR, however, because SGR is applicable to carbonyl compounds that are either susceptible to reduction by SmI_2 or that possess hydroxyl group. Tetrahydrofurylsamarium was found to be the most effective in deprotonating terminal alkynes among various alkylsamariums such as ethyl-, isopropyl-, cyclohexyl-, and cyclopentylsamarium.

Because the reactivity of alkynyl anion generated by the metal–metal exchange toward electrophiles was similar to that formed by reduction of iodoalkynes rather than that of alkynyllithium, the reactive species arising from the metal–metal exchange is most probably an alkynylsamarium. Alkynylsamariums successfully coupled with allyl halides, prenyl bromide, TMSCl, and acetic anhydride as well as carbonyl compounds (under SGR conditions). Diphenyl disulfide, alkyl bromides, acetyl chloride did not undergo coupling. The observed reactivity of alkynylsamariums toward electrophiles is considerably different from that of alkynyllithiums as well as alkylsamariums, and therefore, seems to be synthetically useful to achieve chemoselective alkynylation that cannot be effected by alkynyllithiums. In addition, both the methods using SmI_2 (reduction of alkynyl iodides and deprotonation of alkyne with iodobenzene/THF system) that allow generating alkynylsamariums under non-basic conditions at room temperature are practically useful.

Experimental

General methods

1-Iodoalkynes (**1a**–**c**) were prepared from 1-alkynes according to the previously published procedure.[23] 6-Benzyloxy-1-heptyne[24] was prepared from 5-hexyn-1-ol and benzyl bromide. Ethyl 7-oxooctanoate (**8**),[25] 4-nitrophenyl 3-phenylpropionate,[26] and *O*-(3-phenylpropionyl)-*N*-hydroxysuccinimide[27] were prepared from the corresponding acids by esterification using DCC.[28] SmI_3 was prepared from samarium metal and I_2 prior to use according to the literature.[29] Other chemicals were obtained from commercial sources. Dry benzene, THF, Et_2O was prepared by distillation from sodium/benzophenone prior to use. HMPA was distilled from CaH_2 prior to use. Chemical shifts of ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in ppm (δ) downfield from TMS as an internal standard. Preparative thin-layer chromatography (TLC) was performed on Merck precoated silica gel F-254 plates.

Preparation of SmI_2 in benzene-HMPA

A solution of 1,2-diiodoethane (3.0 g, 10.6 mmol) in benzene (96 mL) containing 10% HMPA (10.7 mL, 57.8 mmol) was added slowly to samarium powder (2.4 g, 16.0 mmol) at 100°C under nitrogen flow. The mixture was refluxed with stirring overnight to give a purple solution. Concentration of the solution was determined by back-titration (treatment with an excess solution of iodine in dry toluene, then the remaining iodine was titrated with sodium thiosulfate).

General procedure for the preparation of 1-iodo-1-alkyne 1-Iodo-1-decyne (1a)

BuLi (1.6 M in hexane, 12.0 mmol) was added to a solution of 1-decyne (10.0 mmol) in THF (20 mL) at −10°C. After 1 h at −10–0°C, iodine (13.0 mmol) dissolved in THF (5 mL) was added dropwise at −78°C, and the reaction mixture was stirred overnight at rt. The reaction mixture was poured into saturated $Na_2S_2O_3$, and extracted with ether. A crude mixture was distilled under reduced pressure to give **1a** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=7.0 Hz), 1.21–1.43 (m, 10H), 1.46–1.56 (m, 2H), 2.35 (t, 2H, J=7.1 Hz); IR (film) 2925, 2856, 2200, 1465 cm^{-1}; Anal. Calcd for $C_{10}H_{17}I$: C, 45.47; H, 6.49. Found: C, 45.22; H, 6.56.

1-Iodo-2-phenylacetylene (1b). A pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.25–7.35 (m, 3H), 7.39–7.46 (m, 2H); IR (film) 2171 cm^{-1}; HRMS calcd for C_8H_5I 227.9436, found 227.9437; Anal. Calcd for C_8H_5I: C, 42.14; H, 2.21. Found: C, 41.96; H, 2.27.

1-Iodo-3-cyclopentylpropyne (1c). A colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.19–1.30 (m, 2H), 1.48–1.69 (m, 4H), 1.73–1.83 (m, 2H), 2.04 (sept, 1H, J=7.0 Hz), 2.36 (d, 2H, J=7.0 Hz); IR (film) 2184, 2152 cm^{-1}; HRMS calcd for $C_8H_{11}I$ 234.9906, found 233.9886.

General procedure for samarium Barbier reactions. 5-Butyl-6-pentadecyn-5-ol (3)

A mixture of **1a** (21.2 mg, 0.080 mmol) and **2** (17.2 mg, 0.12 mmol) in benzene (1.5 mL) was added to SmI_2 in benzene (3 mL of 0.11 M solution, 0.32 mmol) containing HMPA (291 μL, 1.62 mmol) at rt. After 25 min, the reaction mixture was poured into aqueous $NaHCO_3$ solution and extracted with ether. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated. Purification of the residue by preparative TLC (hexane/AcOEt=8:2) gave 17.6 mg (0.063 mmol, 78% yield) of **3** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=7.0 Hz), 0.92 (t, 6H, J=7.3 Hz), 1.24–1.51 (m, 20H), 1.56–1.63 (m, 4H), 1.81 (br s, 1H), 2.19 (t, 2H, J=7.0 Hz); IR (film) 3415, 2230 cm^{-1}; MS *m/z* 262 [$(M-H_2O)^+$]; Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.08; H, 12.69.

5-Benzyl-6-pentadecyn-5-ol. A pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, J=7.1 Hz), 0.93 (t, 3H, J=7.3 Hz), 1.20–1.70 (m, 18H), 1.76 (br s, 1H), 2.16 (t, 2H, J=7.1 Hz), 2.86 (d, 1H, J=13.1 Hz), 2.95 (d, 1H, J=13.1 Hz), 7.23–7.36 (m, 5H); IR (film) 3460 2220 cm^{-1}; HRMS calcd for $C_{22}H_{34}O$ 314.2610, found 314.2605; Anal. Calcd for $C_{22}H_{34}O$: C, 84.02; H, 10.90. Found: C, 83.77; H, 11.05.

4-*t*-Butyl-1-(1-decynyl)cyclohexanol. The stereochemistry of diastereomers is not determined. The major isomer: 61% yield; R_f=0.18 (hexane/AcOEt=9:1); colorless crystals; mp 44.5–45.0°C; ^{1}H NMR ($CDCl_3$) δ 0.87 (s, 9H), 0.88 (t, 3H, J=6.8 Hz), 0.98 (tt, 1H, J=11.9, 3.4 Hz), 1.22–1.55 (m, 16H), 1.68–1.76 (m, 2H), 1.77(br s, 1H), 1.93–2.00 (m, 2H), 2.22 (t, 2H, J=7.0 Hz); IR (KBr) 3247, 2964, 2859, 2240, 1469 cm^{-1}; Anal. Calcd for $C_{20}H_{36}O$: C, 82.13; H, 12.40. Found: C, 81.94; H, 12.21. The minor isomer: 11% yield; R_f=0.42 (hexane/AcOEt=9:1); a colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 9H), 0.88 (t, 3H, J=7.1 Hz), 0.98 (tt, 1H, J=12.1, 3.1 Hz), 1.21–1.42 (m, 12H), 1.43–1.70 (m, 7H), 1.94–2.01 (m, 2H), 2.17 (t, 2H, J=7.1 Hz); IR (film) 3400, 2240 cm^{-1}; HRMS calcd for $C_{20}H_{36}O$ 292.2766, found 292.2748; Anal. Calcd for $C_{20}H_{36}O$: C, 82.13; H, 12.40. Found: C, 81.87; H, 12.36.

3-Butyl-1-phenyl-1-heptyn-3-ol. A pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, 6H, J=7.3 Hz), 1.39 (sext, 4H, J=7.4 Hz), 1.50–1.60 (m, 4H), 1.70–1.77 (m, 4H), 2.02 (s, 1H), 7.27–7.33 (m, 3H), 7.39–7.44 (m, 2H); IR (film) 3390, 2210 cm^{-1}; HRMS calcd for $C_{17}H_{24}O$ 244.1827, found 244.1823; Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.29; H, 9.87.

4-Butyl-1-cyclopentyl-2-octyn-4-ol. A colorless oil; ^{1}H

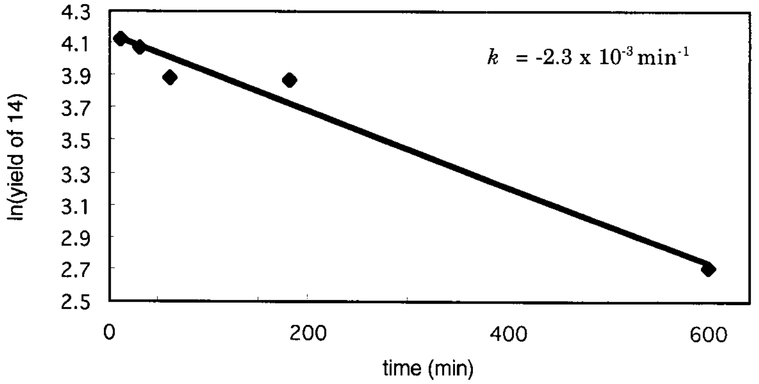


Figure 1. Linear rate plot for the formation of **4** after a definite time stirring of a decynylsamarium intermediate.

NMR ($CDCl_3$) δ 0.92 (t, 6H, J=7.2 Hz), 1.22–1.40 (m, 6H), 1.42–1.68 (m, 12H), 1.72–1.83 (m, 2H), 1.82 (br s, 1H), 1.97–2.09 (m, 1H), 2.20 (d, 2H, J=6.7 Hz); IR (film) 3430, 2230 cm^{-1}; MS m/z 232 [$(M-H_2O)^+$]; Anal. Calcd for $C_{17}H_{30}O$: C, 81.54; H, 12.07. Found: C, 81.45; H, 12.36.

4-Tridecyn-3-ol. A colorless oil; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=7.0 Hz), 1.00 (t, 3H, J=7.4 Hz), 1.21–1.43 (m, 10H), 1.50 (quint, 2H, J=7.4 Hz), 1.63–1.76 (m, 3H), 2.20 (td, 2H, J=7.1, 2.0 Hz), 4.27–4.34 (m, 1H); IR (film) 3360, 2250 cm^{-1}; MS m/z 178 [$(M-H_2O)^+$]; Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.64; H, 12.62.

1-Phenyl-4-tridecyn-3-ol. A colorless oil; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=7.0 Hz), 1.20–1.44 (m, 10H), 1.47–1.56 (m, 2H), 1.75 (d, 1H, J=5.4 Hz), 1.92–2.07 (m, 2H), 2.22 (td, 2H, J=7.1, 2.0 Hz), 2.79 (t, 2H, J=7.9 Hz), 4.32–4.40 (m, 1H), 7.16–7.23 (m, 3H), 7.25–7.31 (m, 2H); IR (film) 2230 cm^{-1}; HRMS calcd for $C_{19}H_{28}O$ 272.2140, found 272.2143; Anal. Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.48; H, 10.34.

Ethyl 7-hydroxy-7-methyl-8-heptadecynoate. A pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=7.0 Hz), 1.26 (t, 3H, J=7.1 Hz), 1.23–1.44 (m, 12H), 1.45 (s, 3H), 1.46–1.70 (m, 8H), 1.84 (s, 1H), 2.18 (t, 2H, J=7.1 Hz), 2.30 (t, 2H, J=7.7 Hz), 4.12 (q, 2H, J=7.1 Hz); IR (film) 3467, 2238, 1737 cm^{-1}; HRMS calcd for $C_{20}H_{36}O_3$ 324.2664, found 324.2646; Anal. Calcd for $C_{20}H_{36}O_3$: C, 74.03; H, 11.18. Found: C, 73.51; H, 11.06.

General procedure for samarium Grignard reactions. 5-Butyl-6-pentadecyn-5-ol (3)

A solution of **1a** (23.4 mg, 0.089 mmol) in benzene (1.0 mL) was added to a solution of SmI_2 in benzene (3 mL of 0.12 M solution, 0.35 mmol) containing HMPA (300 μL, 1.72 mmol) at rt. After 10 min, dry air was introduced until the deep purple color of SmI_2 disappeared, followed by addition of **2** (18.9 mg, 0.13 mmol). The reaction mixture was stirred for 10 min, poured into aqueous $NaHCO_3$ solution, and extracted with ether. Purification of the residue by preparative TLC (hexane/AcOEt=8:2) gave 17.3 mg (0.062 mmol, 70% yield) of **3**. **2-Phenyl-3-dodecyn-2-ol (14):** a yellow oil; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=7.1 Hz), 1.20–1.47 (m, 10H), 1.51–1.59 (m, 2H), 1.74 (s, 3H), 2.27 (t, 2H, J=7.1 Hz), 2.27 (s, 1H), 7.24–7.39 (m, 3H), 7.64–7.68 (m, 2H); IR (film) 3409, 2242 cm^{-1}; MS m/z 240 [$(M-H_2O)^+$]; Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.37; H, 10.42.

1-(1-Decynyl)-2-cyclohexen-1-ol. A colorless oil; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=7.1 Hz), 1.20–1.40 (m, 10H), 1.45–1.54 (m, 2H), 1.71–1.80 (m, 2H), 1.85–1.93 (m, 1H), 1.94 (s, 1H), 1.96–2.06 (m, 3H), 2.20 (t, 2H, J=7.2 Hz), 5.73 (dt, 1H, J=9.9, 1.9 Hz), 5.80 (dt, 1H, J=9.9, 3.5 Hz); IR (film) 3382, 2235, 1648 cm^{-1}; HRMS calcd for $C_{16}H_{24}$ [$(M-H_2O)^+$] 216.1878, found 216.1881; Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.64; H, 11.28.

4-Methyl-5-tetradecyn-1,4-diol. A pale yellow oil; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=7.1 Hz), 1.20–1.42 (m, 10H), 1.45–1.54 (m, 2H), 1.49 (s, 3H), 1.65 (br s, 1H), 1.68–1.93 (m, 4H), 2.18 (t, 2H, J=7.1 Hz), 2.65 (br s, 1H), 3.64–3.79 (m, 2H); IR (film) 3385, 2230 cm^{-1}; MS m/z 207 [$(M-H_2O)^+$]; Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.66; H, 11.99.

Stability of alkynylsamarium. A solution of **1a** (20 mg, 0.08 mmol) in THF (0.5 mL) was added to SmI_2 (0.102 M, 1.4 mL, 0.14 mmol) in THF containing HMPA (137 μL, 0.79 mmol) at 25°C. After a definite time of stirring (10 min, 30 min, 60 min, 180 min, and 600 min), **9** (9.1 mg, 0.08 mmol) was added. The reaction mixture was stirred for 30 min, then poured into water and extracted with ether. The organic layer was washed with water and brine, and dried over $MgSO_4$. The yields of **14** determined by ^1H NMR using dibenzyl ether (5.1 mg, 0.028 mmol) as an internal standard were 62% (10 min), 59% (30 min), 49% (60 min), 48% (180 min), and 15% (600 min), respectively. The half-life period (ln $2/k$) of decynylsamarium was calculated to be 301 min from linear rate plot (Fig. 1).

Coupling reaction of decynylsamarium with various electrophiles

Reactions were conducted by a method similar to that of the SGR.

Tridec-1-en-4-yne.[30] A colorless oil; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=6.8 Hz), 1.21–1.43 (m, 10H), 1.45–1.55 (m, 2H), 2.18 (tt, 2H, J=2.4, 7.0 Hz), 2.91–2.97 (m, 2H), 5.09 (dq, 1H, J=1.8, 10.0 Hz), 5.31 (dq, 1H, J=1.8, 16.9 Hz), 5.83 (ddt, 1H, J=5.2, 10.0, 16.9 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 18.8, 22.7, 23.2, 28.9, 29.1 (2C), 29.2, 31.9, 76.5, 83.0, 115.5, 133.5; IR (film) 1643 cm^{-1}; Anal. Calcd for $C_{13}H_{22}$: C, 87.56; H, 12.44. Found: C, 87.09; H, 12.49.

2-Methyltetradec-2-en-5-yne. A colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, J=6.8 Hz), 1.21–1.40 (m, 10H), 1.43–1.52 (m, 2H), 1.61–1.63 (m, 3H), 1.69–1.71 (m, 3H), 2.14 (tt, 2H, J=2.4, 7.1 Hz), 2.83–2.88 (m, 2H), 5.15–5.21 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.1, 17.6, 17.9, 18.8, 22.7, 25.5, 28.9, 29.1 (2C), 29.2, 31.9, 78.8, 79.9, 120.0, 133.2; IR (film) 2927, 2856, 1456 cm^{-1}; MS m/z (%): 206 (18, M^+), 107 (52), 93 (100).

1-Decynyltrimethylsilane. A colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9H), 0.88 (t, 3H, J=7.0 Hz), 1.20–1.57 (m, 12H), 2.21 (t, 2H, J=7.1 Hz); IR (film) 2175 cm^{-1}; Anal. Calcd for $C_{13}H_{26}Si$: C, 74.20; H, 12.45. Found: C, 74.12; H, 12.72.

Dodec-3-yn-2-one.[31] A colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, 3H, J=6.8 Hz), 1.20–1.45 (m, 10H), 1.53–1.62 (m, 2H), 2.32 (s, 3H), 2.35 (t, 2H, J=7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 14.1, 18.9, 22.6, 27.7, 28.9, 29.0, 29.1, 31.8, 32.8, 81.4, 94.2, 184.9; IR (film) 2210, 1677 cm^{-1}; MS m/z 180 (M^+).

11-Methyl-9,12-henicosadiyn-11-ol. A colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 6H, J=6.9 Hz), 1.21–1.42 (m, 20H), 1.47–1.57 (m, 4H), 1.72 (s, 3H), 2.20 (t, 4H, J=7.2 Hz), 2.32 (s, 1H); IR (film) 3417, 2927, 2856 cm^{-1}; HRMS calcd for $C_{21}H_{35}O$ $[(M-Me)^{\cdot +}]$ 303.2688, found 303.2682.

11-Phenethyl-9,12-henicosadiyn-11-ol. A colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 6H, J=6.8 Hz), 1.20–1.45 (m, 20H), 1.48–1.58 (m, 4H), 2.14–2.20 (m, 2H), 2.24 (t, 4H, J=7.1 Hz), 2.36 (s, 1H), 2.87–2.94 (m, 2H),7.16–7.31 (m, 5H); IR (film) 3426, 3025, 2927, 2856 cm^{-1}; HRMS calcd for $C_{29}H_{44}O$ 408.3392, found 408.3369.

General procedure for the generation of an alkynylsamarium by deprotonation using PhI/SmI$_2$ in THF. 2-Phenyl-3-dodecyn-2-ol (14)

A solution of iodobenzene (88.5 mg, 0.43 mmol) and **15a** (20.0 mg, 0.145 mmol) in THF (0.5 mL) was added to SmI_2 (0.11 M, 7.9 mL, 0.87 mmol) in THF containing HMPA (791 μL, 4.55 mmol) at rt. After 5 min, dry air (ca. 10 mL) was introduced, and then, **9** (52.1 mg, 0.43 mmol) was added. The reaction mixture was stirred for 30 min, quenched with water, and extracted with ether. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated Purification of the residue by preparative TLC (hexane/AcOEt=8:2) gave **14** (30.3 mg, 81% yield).

8-Benzyloxy-2-phenyl-3-octyn-2-ol. A colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.61–1.80 (m, 4H), 1.74 (s, 3H), 2.26 (s, 1H), 2.31 (t, 2H, J=7.0 Hz), 3.50 (t, 2H, J=6.1 Hz), 4.50 (s, 2H), 7.24–7.38 (m, 8H), 7.62–7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.6, 25.4, 29.0, 33.5, 69.8, 70.0, 72.9, 84.1, 85.3, 125.0, 127.5 (2C), 127.6, 128.2, 128.4, 138.6, 146.2; IR (film) 3417, 2240, 1095 cm^{-1}; MS m/z 290 $[(M-H_2O)^+]$; HRMS calcd for $C_{21}H_{24}O_2$ (M^+) 308.1776, found 308.1732; for $C_{20}H_{21}O_2$ $[(M-Me)^{\cdot +}]$ 293.1542, found 293.1533.

2,4-Diphenyl-3-butyn-2-ol. A colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.87 (s, 3H), 2.46 (s, 1H), 7.28–7.35 (m, 4H), 7.36–7.42 (m, 2H), 7.45–7.51 (m, 2H), 7.70–7.76 (m, 2H); IR (film) 3411, 2229 cm^{-1}; Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.15; H, 6.44.

2-Phenyl-4-trimethylsilyl-3-butyn-2-ol. A colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H), 1.75 (s, 3H), 2.35 (s, 1H), 7.26–7.32 (m, 1H), 7.33–7.39 (m, 2H), 7.63–7.68 (m, 2H); IR (film) 3396, 2165 cm^{-1}; Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31. Found: C, 71.78; H, 8.44.

2-Phenyl-5-cyclopentyl-3-pentyn-2-ol. A colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.24–1.36 (m, 2H), 1.49–1.70 (m, 4H), 1.74 (s, 3H), 1.75–1.85 (m, 2H), 2.08 (sept, 1H, J=7.4 Hz), 2.28 (s, 1H), 2.28 (d, 2H, J=6.8 Hz), 7.25–7.30 (m, 1H), 7.32–7.38 (m, 2H), 7.63–7.69 (m, 2H); IR (film) 3407, 2245 cm^{-1}; Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.19; H, 8.75.

General procedure for the generation of an alkynylsamarium by Li^+–Sm^{3+} exchange. 2-Phenyl-3-dodecyn-2-ol (14)

BuLi (1.5 M in hexane, 0.24 mL, 0.36 mmol) was added to **15a** (50.0 mg, 0.36 mmol) in THF (1 mL) at −78°C. After 10 min at −10°C, the reaction mixture was added to SmI_3 (0.41 mmol) in THF (1 mL) containing HMPA (200 μL, 1.15 mmol) at −78°C. After stirring for 30 min −78°C, **9** (19.8 mg, 0.16 mmol) was added. The reaction mixture was allowed to warm to rt, and then, stirred for 30 min. The reaction mixture was quenched, and extracted with ether. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated. Purification of the residue by preparative TLC (hexane/AcOEt=8:2) gave **14** (32.7 mg, 77% yield).

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13. HMPA is essential for the preparation of SmI_2 in benzene[7a] as well as for the reduction of iodoalkynes similarly to the reduction of organohalides.[9b]

14. To eliminate the possibility of Barbier type reaction, excess SmI_2 was decomposed by introducing dry air just before the addition of a ketone while the deep purple of SmI_2 was remained observable after treatment of the halide with SmI_2. If the color of SmI_2 had already disappeared at this point, this step was omitted. Although oxidative decomposition of alkylsamariums has been reported by Molander and McKie (Ref. 3d), the admission of dry air seems to have had a negligible effect on the product yield in our case as similar to the results observed by Hasegawa and Curran (Ref. 3f).

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