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Efficient Preparation of 1,3-Butadiene and Cyclohexene Derivatives Possessing 2-Aminomethyl Group through Indium-Mediated 1,3-Butadien-2-ylation

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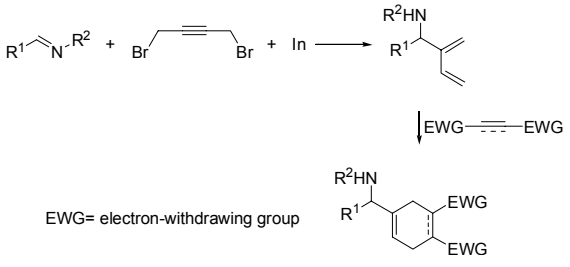
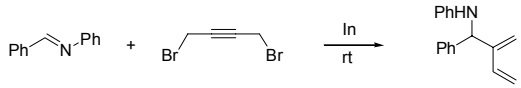
Nucleophilic addition reactions of carbon nucleophiles to imines is essential for synthesizing biologically active heterocyclic compounds.[1] While addition reactions of various carbon nucleophiles to carbonyl compounds have been reported, considerably less successful results were obtained in the analogous addition reactions with imines due to relatively low reactivity of unactivated imines towards nucleophilic addition and deprotonation of imines. During the last decades, various carbon nucleophiles have been used in addition reactions of imines.[2] However, the preparation of 2-aminomethy-1,3-dienes *via* addition reaction of 1,3-butadien-2-yl moiety to imines is still rare. Of these, Grignard cross-coupling reaction of 2-bromo-3-aminopropene with vinyl bromides suffers from poor chemoselectivity.[3] 2-Halomethyl-1,3-diene though quite effective in reacting with 2-amines to give 2-aminomethyl-1,3-dienes are not convenient to prepare.[4] Allene reacts with various amines in the presence of Pd catalysts to give the derivatives of 2-aminomethyl-1,3-diene.[5] Ethylene-alkyne cross metathesis afforded 2-aminomethyl 1,3-dienes.[6] Because so much is now reported about Diels-Alder reaction,[7] we were convinced that when we found a synthetic route to efficient addition reaction of 1,3-butadien-2-yl group to imines, then this reaction would prove useful for the synthesis of 2-aminomethyl-1,3-dienes as well as six-membered carbocycles. Recently, reactions by using organoindiums have been described due to their reactivity, selectivity, ease of preparation and handling, operational simplicity, and low toxicity.[8] On the basis of these properties of organoindiums, we reported Pd-catalyzed cross-couplings, carbonylative cross-couplings, and addition reactions to carbonyl compounds and α,β-enones with allylindiums,[9] allenylindiums,[10] tri(organo)-indiums,[11] tetra(organo)indates,[12] and indium tetra(organothiolates).[13] During the course of this study,[14] we considered the synthetic possibility of 2-aminomethyl-1,3-dienes *via* addition reaction of 1,3-butadien-2-yl moiety[15] to imines by using in situ generated organoindium. Herein, we report addition reactions of 1,3-dien-2-yl indium in situ generated from 1,4-dibromo-2-butyne and indium with imines or the mixture of aldehyde and amine for the synthesis of 2-aminomethyl-1,3-dienes and their application to Diels-Alder reactions for the synthesis of six-membered carbocycles in one-pot process (Scheme 1).



Scheme 1. Selective 1,3-butadien-2-ylation to imines

Addition reactions of organoindiums in situ generated from indium and 1,4-dibromo-2-butyne (**2**)[16] with imine (**1d**) were initially examined (Table 1). The reaction of **1d** with 3 equiv of indium and 1.5 equiv of **2** in THF, DMF, and dioxane did not proceed (entries 1-3). The use of H_2O gave the desired product **3d** in 17% yield and **4d** in 42% yield (entry 4). Although the model reaction produced 1,3-diene **3d** in 32% yield in MeOH, formation of alcohol **4d** (30%) could be unavoidable (entry 6). Therefore, we added the drying agents such as molecular sieve 4 Å and $MgSO_4$ to suppress the hydrolysis of imine **1d** to benzaldehyde (entries 7 and 8). In the case of $MgSO_4$, the yield

Table 1. Optimization of 1,3-butadien-2-ylation to imines with indium and **2**



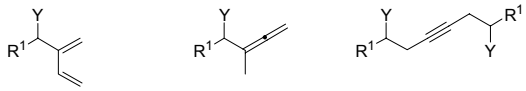
1d **2** **3d**

Entry	Solvent	Additive[a]	In (equiv)	**2** (equiv)	Time (h)	Yield (%)[b]
1	THF		3.0	1.5	20	0
2	DMF		3.0	1.5	20	0
3	Dioxane		3.0	1.5	20	0
4	H_2O		3.0	1.5	3	17(42)
5	H_2O-THF[c]		3.0	1.5	3	15(38)
6	MeOH		3.0	1.5	3	32(30)
7	MeOH	MS-4 Å	3.0	1.5	2	37(25)
8	MeOH	$MgSO_4$	3.0	1.5	2	47(19)
9	EtOH	$MgSO_4$	3.0	1.5	2	70(21)
10	EtOH	$MgSO_4$	2.0	1.0	5	54(21)
11	EtOH	$MgSO_4$	1.3	1.0	5	42(19)
12	EtOH	$MgSO_4$	2.0	1.5	2	86(5)
13	EtOH	$MgSO_4$	2.7	2.0	2	73(18)
14	EtOH	$MgSO_4$-$InCl_3$[d]	2.0	1.5	2	50(38)
15	EtOH	$MgSO_4$-AcOH[e]	2.0	1.5	1	55(15)

[a]1 equiv of $MgSO_4$ was used. [b]Numbers in parentheses indicate yield of **4d**. [c]H_2O:THF = 3:1. [d]20 mol % of $InCl_3$ was used. [e]6 equiv of AcOH was used.

(47%) of **3d** was increased by 15% and formation of alcohol **4d** was suppressed to 19% (entry 8). EtOH was the best solvent among several reaction media examined (THF, DMF, dioxane, H_2O, H_2O-THF, MeOH, and EtOH) (entries 1-9). The present reaction was carried out with 1 equiv of $MgSO_4$ in EtOH, affording the desired product **3d** and **5** in 70% and 21% yields, respectively (entry 9). Stoichiometry of organoindium in situ generated from indium and **2** was investigated (entries 10-13). Of the addition reactions examined, the best results were obtained with 2 equiv of indium and 1.5 equiv of **2** in the presence of 1 equiv of $MgSO_4$ at 25 °C for 2 h in EtOH under a nitrogen atmosphere, producing selectively **3d** in 86% yield (entry 12). The use of indium in less than 2 equiv and **2** in less than 1.5 equiv resulted in a sluggish reaction and provided lower yields as well as longer reaction times (entries 10 and 11). The use of $MgSO_4$-$InCl_3$ and $MgSO_4$-AcOH as an additive produced the desired product **3d** in 50% and 55% yields together with **4d** in 38% and 15% yields, respectively (entries 14 and 15).

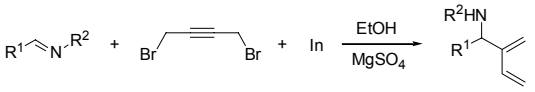
There are no 1,6-diamino-3-hexyne (**6**) and 1,6-dihydroxy-3-hexyne (**7**) *via* 2-butyn-1,4-diylation to imine and aldehyde, respectively, and allenylmethyl amine (**5d**) *via* 1,2-butadien-3-ylation. The ^1H and ^{13}C NMR spectra of **3d** are consistent with benzylphenylamine possessing the 1,3-dien-2-yl group. The four sp^2 resonances (100 MHz) of the 1,3-dien-2-yl group appeared at 145.4, 136.6, 117.8, and 115.1 ppm, indicating that compound **3d** was selectively produced.



R^1= Ph, Y= NHPh (**3d**) R^1= Ph, Y= OH (**4d**) R^1= Ph, Y= NHPh (**5d**) R^1= Ph, Y= NHPh (**6**) R^1= Ph, Y= OH (**7**)

To demonstrate the scope and limitation of the present method, we applied this reaction system to various imine compounds, producing 2-aminomethyl-1,3-dienes (Table 2). Under the optimized conditions, imine **1a** afforded the 1,3-diene **3a** and allenylmethylamine **5a** in 61% and 5% yields, respectively (entry 1). Treatment of **1b** with indium and **2** in the presence of $MgSO_4$ produced the desired product (**3b**) in 60% yield (entry 2). In the case of imine-derived *trans*-cinnamaldehyde, 1,3-diene

Table 2. Selective 1,3-butadien-2-ylation to imines[a]

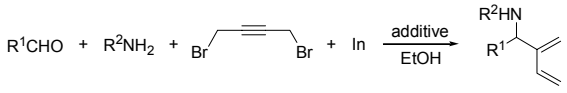


1 **2** **3**

Entry	Imine	R^1	R^2	Time (h)	Product	Yield (%)
1	**1a**	*i*-Pr	Ph	4	**3a**	61(5)[b]
2	**1b**	C_6H_{11}	Ph	7	**3b**	60(4)[c]
3	**1c**	PhCH=CH	Ph	5	**3c**	51
4	**1d**	Ph	Ph	2	**3d**	86(5)[c]
5	**1e**	4-Cl-C_6H_4	Ph	2	**3e**	75(8)[b]
6	**1f**	3-Br-C_6H_4	Ph	3	**3f**	60(9)[c]
7[d]	**1g**	2-I-C_6H_4	Ph	5	**3g**	61(19)[c]
8	**1h**	4-Me-C_6H_4	Ph	2	**3h**	72(7)[b]
9	**1i**	2-Me-C_6H_4	Ph	4	**3i**	67(4)[b]
10[e]	**1j**	3-HO-C_6H_4	Ph	2	**3j**	75(5)[b]
11	**1k**	4-MeO_2C-C_6H_4	Ph	1	**3k**	65(13)[b]
12	**1l**	2-Furyl	Ph	2	**3l**	67(4)[c]
13	**1m**	Ph	4-I-C_6H_4	1	**3m**	74(14)[c]
14	**1n**	Ph	4-MeO-C_6H_4	4	**3n**	76(11)[c]
15	**1o**	Ph	Bn	6	**3o**	62(17)[c]
16[e]	**1p**	EtO_2C	BnO	6	**3p**	77(8)[c]
17[e]	**1q**	EtO_2C	4-MeO-C_6H_4	6	**3q**	65(9)[c]

[a]Reactions were carried out with 1 equiv of **1**, 1.5 equiv of **2**, 2 equiv of indium in the presence of 1 equiv of $MgSO_4$ at rt. [b]**5** Derivatives. [c]**4** Derivatives. [d]Indium:**2** = 3:2.3. [e]3 equiv of indium was used.

Table 3. 1,3-Butadien-2-ylation using aldehydes, amines, and organoindiums in one-pot[a]



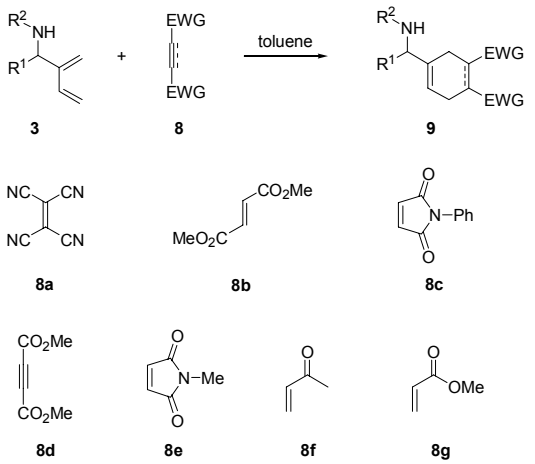
2 **3**

Entry	R^1	R^2	Additive	Time (h)	Product	Yield (%)[g]
1	Ph	Ph[b]	$MgSO_4$	3	3d	50(18)
2	Ph	Ph[b]	$MgSO_4$-$InCl_3$[c]	3	3d	60(12)
3	Ph	Ph[b]	$MgSO_4$[d]	3	3d	40(23)
4	Ph	Ph[b]	MS-4 Å	3	3d	54(18)
5	Ph	Ph	AcOH	2	3d	64(8)
6	Ph	Ph	AcOH[e]	2	3d	49(20)
7	Ph	Ph	AcOH[f]	2	3d	63(9)
8	C_6H_{11}	Ph	AcOH	6	3b	48(23)
9	Ph	4-MeO-C_6H_4	AcOH	6	3n	56(19)
10	4-Cl-C_6H_4	Ph	AcOH	5	3e	65(10)
11	3-HO-C_6H_4	Ph	AcOH	5	3j	59(12)
12	4-MeO_2C-C_6H_4	Ph	AcOH	1	3k	58(18)

[a]Reactions were carried out with 1 equiv of aldehydes, 1.5 equiv of amines, 1.5 equiv of **2**, and 2 equiv of indium in the presence of 1 equiv of $MgSO_4$ or 1 equiv of AcOH at rt. [b]1 equiv of amine was used. [c]20 mol % $InCl_3$ were used. [d]3 equiv of $MgSO_4$ were used. [e]0.5 equiv of AcOH were used. [f]2 equiv of AcOH were used. [g]Numbers in parentheses indicate yields of **4**.

3c was obtained in 51% yield (entry 3). The presence of either an electron-donating or electron-withdrawing group, such as chloride, bromide, iodide, methyl, hydroxyl, and methoxycarbonyl groups, on the aromatic ring had little affect the efficiency and selectivity of indium-mediated 1,3-butadien-2-ylation of imine (entries 5-11). Treatment of imine **1e** and **1f** with organoindium in the presence of $MgSO_4$ gave rise to the 1,3-dienes (**3e** and **3f**) in 75% and 60% yields, respectively (entries 5 and 6). Imine **1g** reacted with 3 equiv of indium and 2.3 equiv of **2** to afford 1,3-diene **3g** in 61% yield (entry 7). 1,3-Butadien-2-yl indium smoothly added to imines **1h** and **1i** to provide 1,3-dienes **3h** and **3i** in 72 and 67% yields, respectively (entries 8 and 9). It is noteworthy that protection of a hydroxyl group on substrates is not necessary as demonstrated by the reaction of imine **1j** (entry 10). Imine **1k** bearing a 4-methoxycarbonyl group turned out to be compatible with the present reaction conditions (entry 11). 2-Furfural worked equally well with the employed reaction conditions, producing the 1,3-diene **3l** in 67% yield (entry 12). Altering the electron demand of the substituents on aryl rings of anilines produced the 2-aminomethyl-1,3-dienes in good yields together with 1,3-butadien-2-yl methanols in about 10% yields (entries 13-15). Subjecting imines **1m** and **1n** to the organoindium resulted in **3m** and **3n** in 74% and 76% yields, respectively (entries 13 and 14). Reaction of glyoxylic oxime ether **1p** and glyoxylic imine **1q** with 3 equiv of indium and 1.5 equiv of **2** provided *N*-protected α-amino esters **3p** and **3q** having the 1,3-diene group in 77% and 65% yields, respectively (entries 16 and 17).

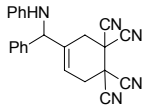
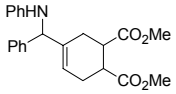
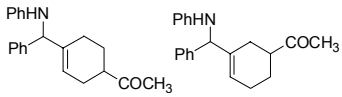
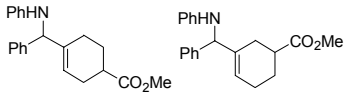
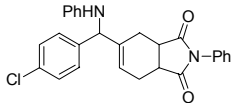
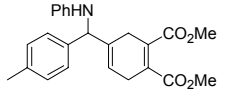
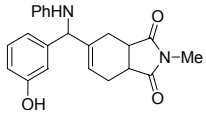
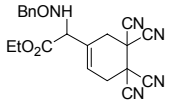
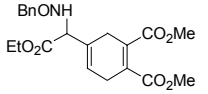
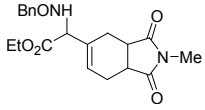
Next, three component reactions of aldehydes, amines, and organoindiums were investigated in one-pot process (Table 3). The three components reaction of benzaldehyde, aniline, and organoindium in situ generated from 2 equiv of indium and 1.5 equiv of **2** in the presence of 1 equiv of $MgSO_4$ has been carried out at 25 °C for 3 h in EtOH under a nitrogen atmosphere, affording selectively the desired product **3d** (50%) together with **4d** (18%) (entry 1). A variety of additives such as $MgSO_4$, $MgSO_4$-$InCl_3$, 4 Å molecular sieve, and AcOH were examined to increase the product yield as well as suppress **4d**. Of the additives examined, 1 equiv of AcOH gave the best result (entry 5).



Scheme 2. Diels-Alder reactions of 2-aminomethyl-1,3-dienes with dienophiles

Under the optimum conditions, the desired product **3d** was produced in 64% yield. Treatment of cyclohexanecarbaldehyde and aniline with indium and **2** afforded **3b** in 48% yield in one-pot process (entry 8). In situ generated imine **1n** was readily 1,3-butadien-2-ylated with organoindium to provide **3n** in 56% yield (entry 9). We were pleased to obtain **3e** and **3j** in 65% and 59% yields, respectively, from three component reactions

Table 4. Diels-Alder reactions of 2-aminomethyl-1,3-dienes with dienophiles[a]

Entry	Reactant	Temp (°C)	Time (h)	Product	Yield (%)[b]
1	**3d/8a**	25	3		**9a** 85
2	**3d/8b**	100	2		**9b** 95(1:1.4)
3	**3d/8f**	100	2		**9c** 72(1:1.8) **9d** 10(1:1)
4	**3d/8g**	100	5		**9e** 63(1:1.5) **9f** 18(1:1)
5	**3e/8c**	25	5		**9g** 89(1:1.5)
6	**3h/8d**	100	2		**9h** 80
7	**3j/8e**	25	10		**9i** 82(1:1.6)
8	**3q/8a**	25	2		**9j** 76
9	**3q/8d**	80	3		**9k** 62
10	**3q/8e**	25	5		**9l** 83(1:1.1)

[a]1 equiv of **3** and 2 equiv of dienophiles were used. [b]Ratios in parentheses indicate diastereomeric ratio.

in one-pot process (entries 10 and 11). In the case of methyl 4-formylbenzoate, the desired product **3k** was produced in 58% yield together with **4k** in 18% yield (entry 12). Although treatment of indium and **2** with a mixture of aldehydes and amines gave an inferior result in terms of the chemical yields, the present method efficiently assembled three components in one-pot process, producing the 2-aminomethyl-1,3-dienes in good yield.

Encouraged by these results, we were convinced that reaction of a variety of 2-aminomethyl-1,3-dienes **3** with dienophiles **8** would prove useful for the synthesis of six-membered carbocycles (Scheme 2). The results are summarized in Table 4. First, 1,3-diene **3d** was treated with 2 equiv of tetra(cyano)ethylene (**8a**) and dimethyl fumarate (**8b**) to afford **9a** and **9b** in 85% and 95% (dr = 1:1.4) yields, respectively (entries 1 and 2). The use of methyl vinyl ketone (**8f**) provided the adduct **9c** (dr = 1:1.8) and **9d** (dr = 1:1) in 72% and 10% yields, respectively, at 100 ^{o}C for 2 h (entry 3). Also, reaction worked equally well with 1,3-diene **3e** and *N*-phenylmaleimide (**8c**), producing **9g** in 89% (dr = 1:1.5) yield (entry 5). We were pleased to obtain **9h** and **9i** in 80% and 82% yields, respectively, from the reaction of **3h** and **3j** with **8d** and **8e** (entries 6 and 7). Next, subjecting 1,3-diene **3q** having amino ester group to 2 equiv of **8a**, **8d**, and **8e** produced adduct **9j** (76%), **9k** (62%), and **9l** (83%), respectively (entries 8-10).

In summary, we have developed a efficient method for the synthesis of a variety of 2-aminomethyl 1,3-dienes through the reactions of imines with organoindium in situ generated from indium and 1,3-dibromo-2-butyne. Three component reactions of aldehydes, amines, and organoindium gave the successful results in one-pot process. In addition, Diels-Alder reactions of 1,3-dienes possessing aminemethyl group with dienophiles provided valuable adducts including α-amino esters having 6-membered carbocycles at α-position.

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