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Synthetic Strategy for Functionalized Polyacene Structure Using Nickel-Catalyzed Alkynylstannylation of 1,2-Dienes

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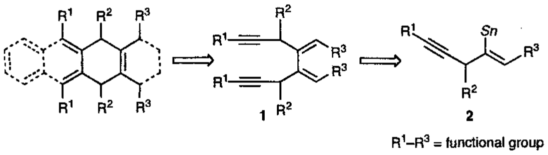
Polyacene structures, linearly-fused six membered-rings, were readily prepared by various modes of cyclization of 2,3-bis(alkynylmethyl)-1,3-butadienes, which were synthesized through the nickel-catalyzed alkynylstannylation of 1,2-dienes followed by the palladium-catalyzed oxidative homocoupling of the resulting alkenylstannanes.

Key words: polyacene, carbostannylation, nickel, 1,2-diene, alkynylstannane

1. INTRODUCTIOM

Polyacenes, conjugated linearly fused benzene-rings, have acquired growing importance as organic conductive materials due to their low band gap.[1] Although simple polyacenes are readily available, functionalized ones are hardly accessible due to lack of reliable synthetic route. Generally, parent acenes are poorly soluble to organic solvents, and thus difficult to be fabricated. Furthermore, higher members of acenes are unstable owing to oxidizable π-electrons spreading on their aromatic rings. Thus, heptacene has been the longest isolable one with no substituent.[1a] Although introduction of a functional group to acenes is expected to solve these drawbacks, no general methods are available. 2,3-Bis(alkynylmethyl)-1,3-butadienes **1** in Scheme 1 should be one of versatile precursors of acene structures having functional groups. The diene and diyne can undergo cyclization with unsaturated compounds through cycloaddition and transition metal-mediated reactions, respectively. Although homocoupling of α-(alkynylmethyl)-vinylstannane **2** might readily afford **1**, no convenient method has been available to synthesize alkenylstannane **2** having such a labile functional group as a carbon–carbon triple bond. We have disclosed a series of carbostannylations of alkynes catalyzed by a palladium or a nickel complex to give vinylstannanes substituted by an alkynyl, alkenyl, allyl or acyl group,[3] and have found that acylstannylation of 1,2-dienes proceeds smoothly in the presence of a catalytic amount of a nickel complex to give α-(acylmethyl)vinylstannanes.[4,5] Herein we disclose that a nickel complex catalyzes the alkynyl-stannylation of 1,2-dienes to give α-(alkynylmethyl)vinylstannanes, which are convertible to various acene structures via the palladium-catalyzed oxidative homocoupling reaction and cyclization reactions.[6]

Scheme 1



2. ALKYNYLSTANNYLATION OF 1,2-DIENES

We first examined the addition of trimethyl-(phenylethynyl)tin (**3a**) with allene (**4a**) under the conditions similar to those for the nickel-catalyzed acylstannylation of allene (5 mol% of Ni(cod)$_2$, no ligand) and were disappointed by the formation of a complex mixture of products. Thorough investigation of the reaction conditions showed us that bisphosphines having a three-carbon linkage were crucial for the alkynyl-stannylation. For example, treatment of **3a** with 5 mol% of Ni(cod)$_2$–1,3-bis(diphenylphosphino)-propane (DPPP) under an atmosphere of **4a** in toluene at 30 °C for 10 h gave 5-phenyl-2-tri-methylstannyl-1-penten-4-yne (**5aa**) in 63% yield (Eq. 1, Table I, entry 1). The reaction of tri-methyl(triethylsilylethynyl)tin proceeded in a similar manner, and alkenylstannane **5ba** was obtained in 90% yield (entry 2). The addition of alkynyl and stannyl groups took place predominantly at the internal double bond of 1,2-heptadiene to give **5ab** as the major product (entry 3). This catalyst was applicable also to alkynylstannylation of *tert*-butylallene to give **5ac** exclusively (entry 4). On the other hand, linear-(*Z*)-alkenylstannane (**6ac**) was obtained as a major product when we switched the ligand to 1,3-bis(dimethyl-phosphino)propane (DMPP) (entry 5). Thus, two different alkenylstannanes are prepared by properly choosing a ligand.

Allenes with two substituents at 1,3- and 1,1-positions were also applicable to this reaction.

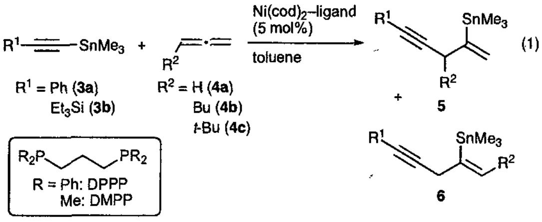
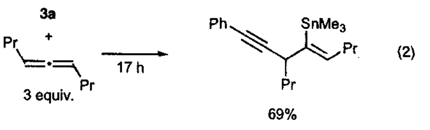


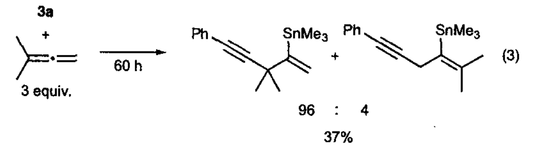
Table I. Alkynylstannylation of 1,2-Dienes[a]

entry	ligand	R^1	R^2	temp (°C)	time (h)	yield[b] (%)	**5** : **6**[c]
1[d]	DPPP	Ph	H	30	10	63	– (**5aa**)
2[d]	DPPP	Et_3Si	H	50	24	90	– (**5ba**)
3	DPPP	Ph	Bu	30	10	72	85(**5ab**) : 15(**6ab**)
4	DPPP	Ph	*t*-Bu	50	70	57	98(**5ac**) : 2(**6ac**)
5[e]	DMPP	Ph	*t*-Bu	50	49	66	14(**5ac**) : 86(**6ac**)

[a] Reaction was carried out using an alkynylstannane (0.20 mmol), a 1,2-diene (0.60 mmol), $Ni(cod)_2$ (10 μmol) and a ligand (10 μmol) in toluene. [b] Isolated yield of **5** and **6** based on an alkynylstannane. [c] Determined by ^{119}Sn NMR. [d] Reaction was carried out under allene atomosphere (1 atm). [e] 0.30 mmol of *tert*-butylallene was used.

Thus, **3a** reacted with 4,5-nonadiene to give (*Z*)-alkenylstannane as a sole product (Eq. 2). 1,1-Dimethylallene reacted with **3a** to afford a branched product exclusively albeit in low yield (Eq. 3).



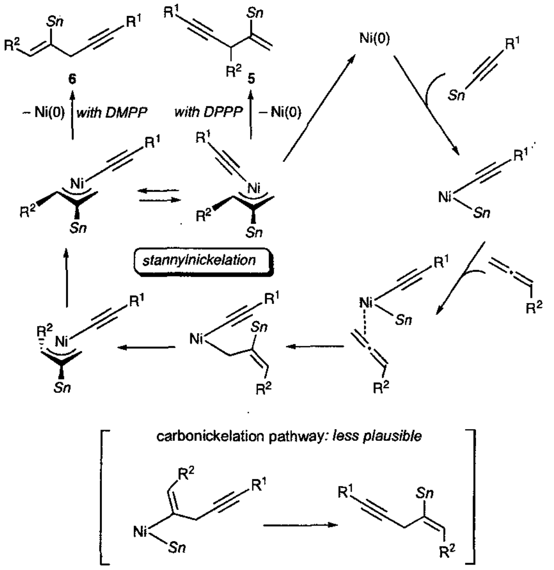


Conditions: $Ni(cod)_2$–DPPP (5 mol %), toluene, 50 °C

3. MECHANISM

A plausible reaction mechanism is shown in Scheme 2. The reaction should be initiated by oxidative addition of a C–Sn bond of the alkynylstannane to a nickel(0) complex. Then 1,2-diene should insert into a Ni–Sn bond to afford a σ-allylnickel intermediate. This intermediate is ready to isomerize to *syn*-π-allylnickel via *anti*-π-allylnickel complex. With a DPPP ligand, reductive elimination occurs from the *syn*-π-allylnickel complex, where an alkynyl group is *cis* to a substituted carbon of π-allyl group, to give a branched product **5** and a nickel(0), while DMPP favors reductive elimination from the corresponding *trans*-isomer to form (*Z*)-linear product **6**. At present, it is not clear how these two ligands distinguish between these two pathways. Insertion of a 1,2-diene into Ni–C bond is unlikely, since the product of this route should be an (*E*)-linear alkenylstannane derived from an (*E*)-alkenylnickel intermediate.

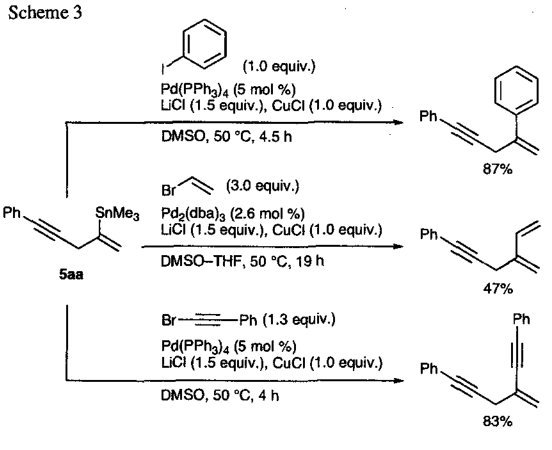
Scheme 2



4. TRANSFORMATIONS OF PRODUCTS

Alkynylstannylation products can naturally be applied to the palladium-catalyzed cross-coupling reaction with various organic halides.[7] Actually, iodobenzene, vinyl bromide and 1-bromo-2-phenylethyne reacted with **5aa** to give various alkynylmethyl substituted conjugated compounds (Scheme 3).

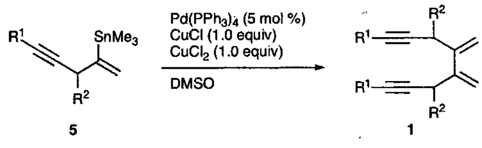
Scheme 3



As expected, 2,3-bis(alkynylmethyl)-1,3-butadienes **1** were readily obtained by the oxidative homocoupling of the alkynyl-stannylation products (Scheme 4). Thus, the palladium-catalyzed reaction of **5** with a stoichiometric amount of $CuCl/CuCl_2$[8] afforded the corresponding dienediyne **1** in a good yield. The reaction of **5ab** gave a mixture of *dl* and *meso* **1ab** in a nearly 1:1 ratio.

Various 2,3-bis(alkynylmethyl)-1,3-butadienes **1** in hand, we first examined construction of functionalized anthracene structures (Scheme 5). Thus, 2,3-bis(phenylethynylmethyl)-1,3-butadiene (**5aa**) was treated with Cp_2ZrBu_2 followed

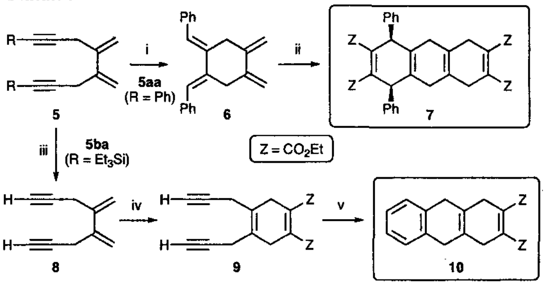
Scheme 4



R^1	R^2		temp	time	yield
Ph	H	(**5aa**)	50 °C	2 h	86% (**1aa**)
Et_3Si	H	(**5ba**)	40 °C	0.8 h	73% (**1ba**)
Ph	Bu	(**5ab**)	50 °C	3 h	82% (**1ab**) (*dl*:*meso* = ca. 1:1)

by treatment with CuCl and *N*,*N*′-dimethylpropyleneurea (DMPU) gave a bis-1,3-diene product **6**. Both the 1,3-diene moieties were successfully converted to two six-membered rings by the Diels-Alder reaction to afford functionalized anthracene structure **7**.[9] On the other hand, triethylsilyl group of 2,3-bis-(trimethylsilylethynylmethyl)-1,3-butadiene (**5ba**) was removed upon treatment with tetrabutylammonium fluoride to give **8**,[10] which reacted with diethyl acetylenedicarboxylate in a Diels-Alder manner to give annulation product **9** quantitatively. The remaining endiyne part was treated with acetylene in the presence of a nickel catalyst to give another functionalized anthracene structure **10**.[11]

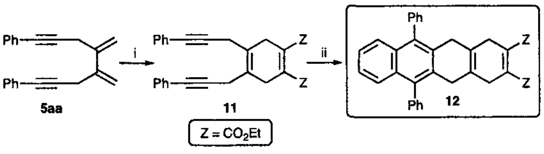
Scheme 5



Reagents and conditions: i, $CpZrBu_2$ (2.0 equiv.), THF, –78 °C, 1 h then r.t., 1 h, then CuCl (4.3 equiv.), *N*,*N*′-dimethylpropyleneurea (6.0 equiv.), r.t., 2 h, 55%; ii, $EtO_2CC{\equiv}CCO_2Et$ (8.0 equiv.), toluene, 100 °C, 28 h, 70%.; iii, Bu_4NF (4.0 equiv.), AcOH (5.2 equiv.), THF, r.t., 44 h, 92%.; iv, $EtO_2CC{\equiv}CCO_2Et$ (5.0 equiv.), toluene, 100 °C, 23 h, 100%.; v, $Ni(acac)_2$ (30 mol %), $(i\text{-}Bu)_2AlH$ (60 mol %), PPh_3 (1.2 equiv.), $HC{\equiv}CH$ (1 atm), THF, r.t., 21 h, 56%

Next, we examined construction of the diphenyl-substituted tetracene structure (Scheme 6). Thus, **5aa** was first allowed to react with diethyl acetylenedicarboxylate similarly to give dihydrobenzene **11** in 84% yield. Then, this complex was treated with Cp_2ZrBu_2 complex followed by *o*-diiodobenzene, CuCl, and DMPU to afford diphenyl-substituted tetracene structure **12**.[12]

Scheme 6



Reagents and conditions: i, $EtO_2CC{\equiv}CCO_2Et$ (5.0 equiv.), toluene, 100 °C, 28 h, 84%.; ii, Cp_2ZrBu_2 (1.7 equiv.), THF, –78 °C, 1 h then r.t., 1 h, then *o*-$I_2C_6H_4$ (3.0 equiv.), CuCl (3.9 equiv.), *N*,*N*′-dimethylpropyleneurea (5.1 equiv.), 50 °C, 15 h, 40%.

5. CONCLUSION

In conclusion, we have demonstrated the nickel-catalyzed alkynylstannylation of 1,2-dienes and their application to the synthesis of several functionalized acene structures through oxidative homocoupling and various cyclization reactions. Substitution patterns of alkynylstannylation products are controllable by choosing a proper ligand, and the reaction tolerates various functional groups. Thus, we expect that this strategy would be applicable to diverse kinds of functionalized acene structures.

6. ACKNOWLEDGMENT

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