DOI: 10.1002/adsc.201601400

Advanced Synthesis & Catalysis

Olefin-Migrative Cleavage of Cyclopropane Rings through the Nickel-Catalyzed Hydrocyanation of Allenes and Alkenes

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Received: December 21, 2016; Revised: January 18, 2017; Published online: ■■ ■■, 0000

Supporting information for this article can be found under http://dx.doi.org/10.1002/adsc.201601400.

Abstract: A nickel-catalyzed hydrocyanation triggered by hydronickelation of the carbon-carbon double bonds of allenes followed by cyclopropane cleavage is described. The observed regio- and stereochemistries in the products are strongly influenced by the initial hydronickelation step, and allenyl- and methylenecyclopropanes reacted smoothly to promote the cleavage of cyclopropane. In contrast, this cleavage was not observed with vinylidenecyclopropanes, because the initial hydronickelation does not give a suitable intermediate for cleavage of the cyclopropanes.

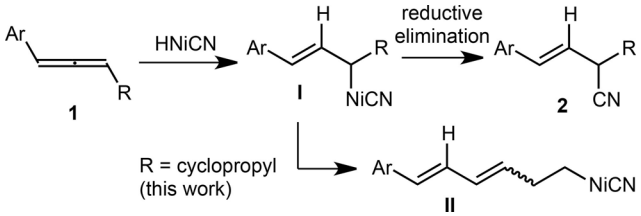
Keywords: allenes; cyclopropanes; homogeneous catalysis; hydrocyanation; nickel

Introduction

Since the cyano group is a versatile functionality that is equivalent to a carboxyl, formyl, amino or hydroxymethyl group, its introduction, particularly by a catalytic protocol, has been an important topic in synthetic chemistry. The pioneering work on the installation of a cyano group under transition metal catalysis concerned the hydrocyanation of carbon-carbon multiple bonds,[1] and this reaction represented a breakthrough for the introduction of heteroatoms through the cleavage of X–CN bonds (X = Si,[2] Ge,[3] Sn,[4] S,[5] B,[6] C,[7,8] N,[9] O[10] Br[11]) under nickel and palladium catalysis.

Among the existing examples of nickel-catalyzed hydrocyanation, a wide variety of substrates such as olefins,[12] conjugated dienes,[13] alkynes[14] and allenes[15] has been used. However, the regio- and stereoselectivities observed in these transformations have not been satisfactory, except for vinylarenes[16] and cyclization reactions.[8a–d] To achieve a higher level of regioselectivity in hydronickelation, we focused on the unique reactivity of cyclopropylallenes.

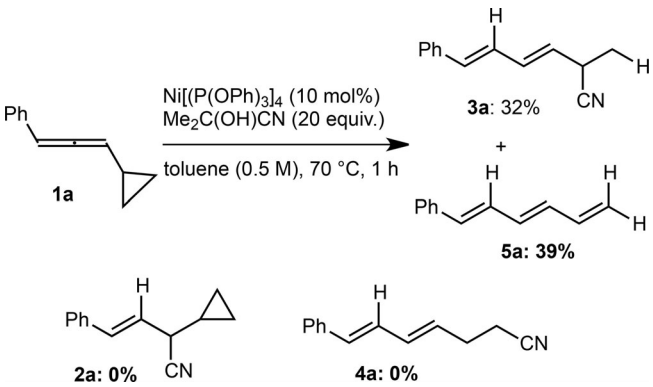
Allenes (1,2-diene, C=C=C)[17] are among the most useful substrates because the selective functionalization of two different C=C double bonds can provide a wide variety of products through a single transformation. We have recently established a regio- and stereoselective hydrocyanation of 1,3-disubstituted allenes and revealed that the aryl groups in **1** play a key role in determining the regiochemistry of **2** in the C–CN bond formation step. (Scheme 1).[18] This result prompted us to design and generate an alternative intermediate. If regioselective C–C σ-bond cleavage (R = cyclopropyl) before reductive elimination from **I** is favored, a primary organonickel species (**II**) would be provided. In the present work, we have generated this species and report the details of this unprecedented nickel-catalyzed hydrocyanation.



Scheme 1. Hydrocyanation of aryl-substituted allenes (**1**).

Results and Discussion

First, we investigated the reaction of 3-cyclopropyl-1-phenyl-1,2-propadiene (**1a**) in the presence of 10 mol% of $Ni[P(OPh)_3]_4$ with acetone cyanohydrin [$Me_2C(OH)CN$] as the HCN source at 70 °C in toluene (Scheme 2). Both **3a** and **5a** were obtained as

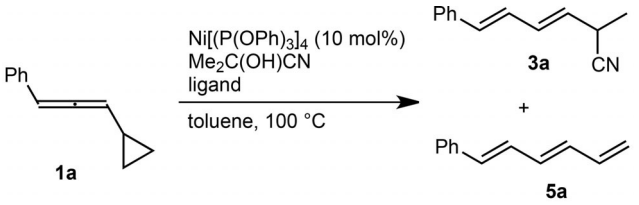


Scheme 2. Catalytic hydrocyanation of **1a**.

a result of cyclopropane cleavage, however, the simple HCN adduct (**2a**) and primary carbonitrile (**4a**) were not produced at all. This result suggests that the intermediate **II** in Scheme 1 can be generated as a precursor of **5a** and cyclopropane cleavage would be much faster than reductive elimination of **I** because **2a** was not observed at all. The formation of **4a** would be disfavored due to rapid β-hydride elimination (β-H elim.) to **5a** from **II**.

To better understand the hydrocyanation of **1a**, the effects of reaction parameters, such as reaction temperature, concentration and ligands, were studied (Table 1). Although the ratio of **3a**/**5a** was not influenced by an increased temperature of 100 °C (entry 1), formation of **5a** was decreased in the case of a higher concentration (entry 2). The addition of $P(OPh)_3$ enhanced the reaction efficacy to give **3a** in 72% yield along with **5a** in 10% yield (entry 3), however a reduced amount of $Me_2C(OH)CN$ gave a lower yield of **3a** (entry 4). In the case of TMSCN as cyano source instead [with MeOH and $P(OPh)_3$ (50 mol%), toluene (1.0 M), 100 °C, 1 h], 54% of **3a** was obtained. With the use of various phosphines or phosphites instead of $P(OPh)_3$, neither the yield of **3a** nor the ratio of **3a**/**5a** was improved (entries 6–9). Bidentate phosphine ligands such as dppe, dppp, dppb and xantphos did not improve the product ratio (entries 10–13). Thus, the optimized conditions in entry 3 were used for further investigation.

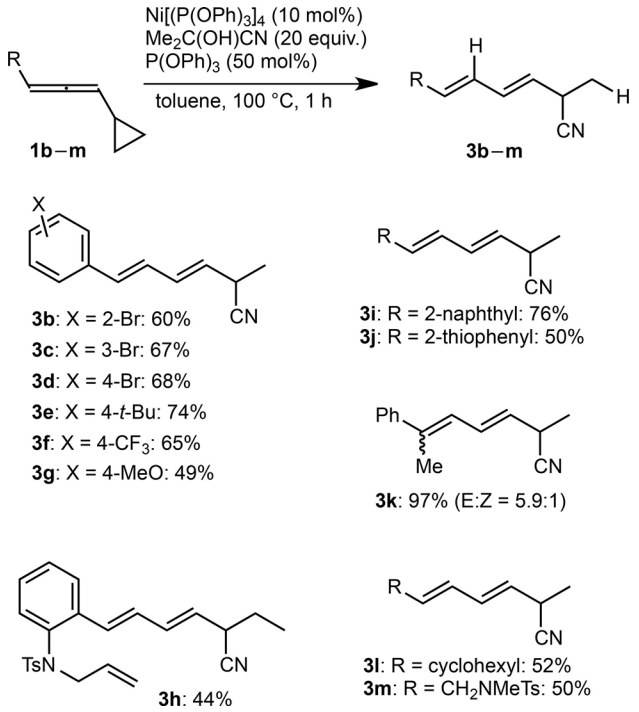
Table 1. Optimization of the hydrocyanation reaction using **1a**.



Entry	$Me_2C(OH)CN$ [equiv.]	Ligand [mol%]	Toluene (M)	Time [h]	Yield **3a** [%][a]	Yield **5a** [%][a]
1	20	-	0.5	1	40	45
2	20	-	1.0	1	47	9
3	20	$P(OPh)_3$ (50)	1.0	1	72	10
4	10	$P(OPh)_3$ (50)	1.0	1	67	8
5	20	PPh_3 (50)	1.0	1	40	39
6	20	$P(4\text{-}MeOC_6H_4)_3$ (50)	1.0	1	15	60
7	20	$P(4\text{-}CF_3C_6H_4)_3$ (50)	1.0	1	40	0
8	20	$P(OMe)_3$ (50)	1.0	1	59	0
9	20	$P(OEt)_3$ (50)	1.0	1	13	51
10	10	dppe (25)	1.0	2	21	14
11	10	dppp (25)	1.0	2	42	18
12	10	dppb (25)	1.0	2	40	29
13	10	xantphos (25)	1.0	2	39	20

[a] Isolated yields.

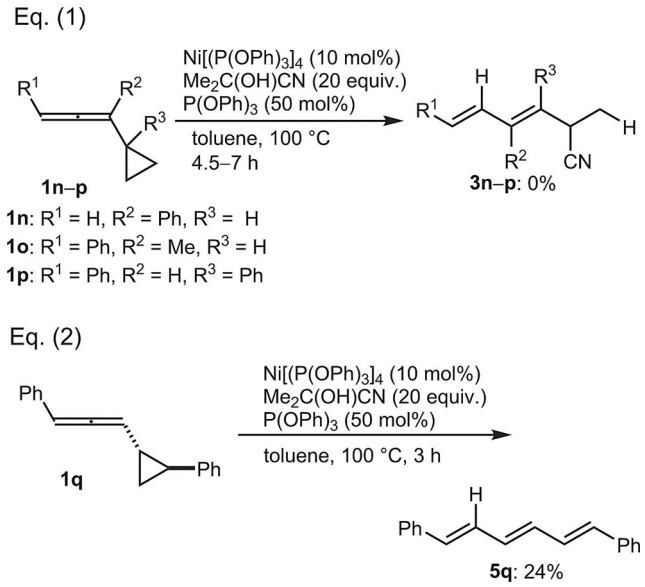
We next examined the use of various substrates (**1b**–**m**) (Scheme 3). The spectrum of substituents on the benzene ring showed that this reaction could accommodate a wide range of substrates. For example, 2-, 3- and 4-bromo substituents (**1b**–**d**) did not influence the conversion to the corresponding adducts **3b**–**d** in respective yields of 60–68% as sole products. Alkyl substituents such as *tert*-butyl and CF_3 groups also gave **3e** and **3f** in moderate yields of 74% and 65%, respectively, however methoxy and *N*-allylsulfonylamino groups decreased the yield of **3g** and **3h** to 49% and 44%, respectively. Further transformation by thermal [4+2] cycloaddition of **3h** was unsuccessful. Other aromatic moieties such as β-naphthyl and 2-thiophene could be converted to the single products **3i** and **3j** in respective yields of 76% and 50%. Trisub-



Scheme 3. Substrate scope for hydrocyanation of **1b**–**m**.

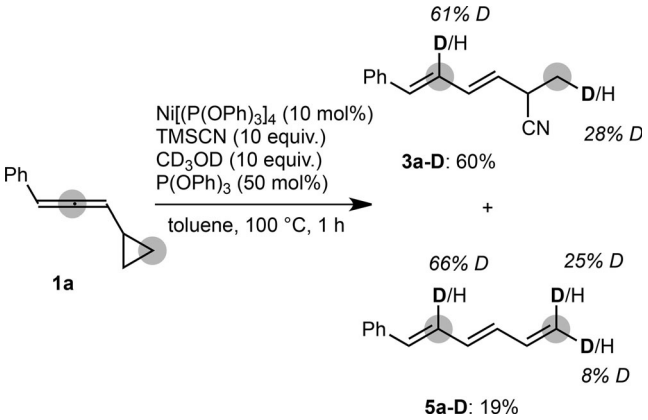
stituted allene (**1k**) was reactive enough to be transformed to **3k** in 97% yield with a mixture of stereoisomers. In the case of alkyl substituents such as **1l** and **1m**, the corresponding adducts were also obtained in a regio- and stereoselective manner.

The substrate **1n–p** were all inert in the reaction even with reaction times of 4.5 h or longer [Scheme 4, Eq.(1)]. In the case of phenyl-substitution on a cyclopropane ring (**1q**), the conjugated triene (**5q**) was obtained as a sole product through the cleavage of the more substituted C–C bond in the cyclopropane ring [Scheme 4, Eq. (2)].

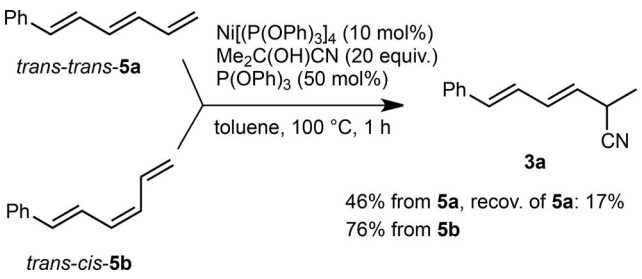


Scheme 4. Attempted hydrocyanation of **1n–q**.

To elucidate the reaction pathway, we next examined the reaction with DCN generated from TMSCN with CD_3OD (Scheme 5). As expected, D atoms were incorporated into the respective gray-shaded carbons in **1a** and **3a-D** (olefinic in 61% D and methyl in 28% D) together with **5a-D** (olefinic in 66% and methylene in 33%) in respective yields of 60% and 19%. Both products showed a similar incorporation of D with respect to its positions and ratio, which strongly suggests that **3a-D** would be obtained from **5a-D**. We next investigated hydrocyanation using both isomeric trienes (**5a** and **5b**) independently to evaluate their behavior and reactivity (Scheme 6). Although they showed different reactivities, both gave **3a** as a sole HCN adduct under the optimum conditions. Thus, we concluded that **5a** is a precursor of **3a**.[19]

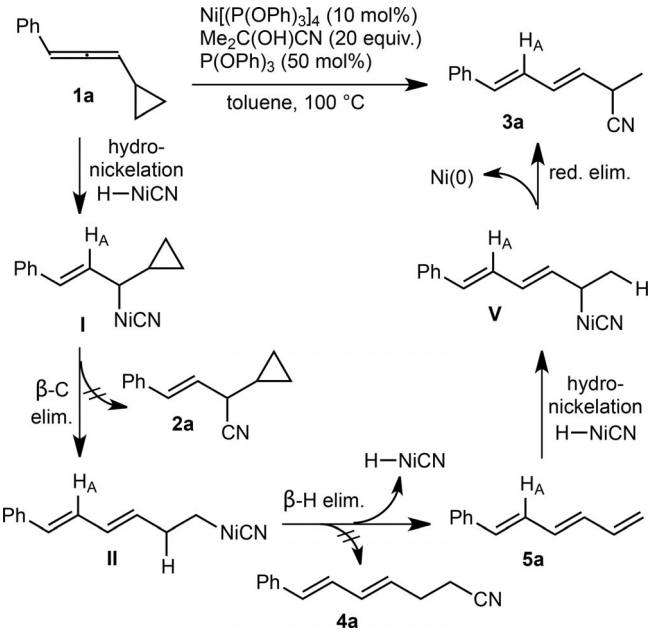


Scheme 5. Hydrocyanation of **1a** using DCN.



Scheme 6. Hydrocyanation of **5**.

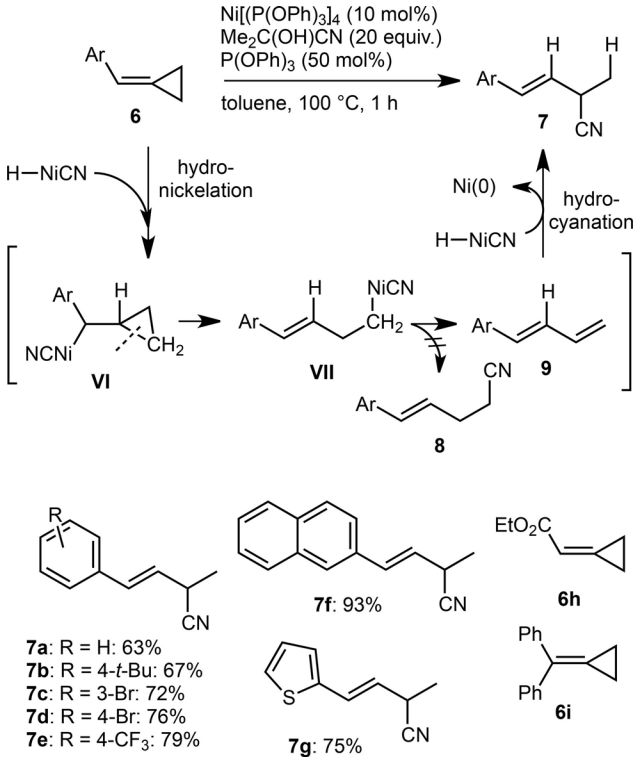
Based on these results, we can propose the plausible reaction mechanism shown in Scheme 7. The regiochemistry of the initial hydronickelation determines the reaction pathway; initial C–H bond formation favorably occurs at the *sp* carbon to promote subsequent β-carbon elimination (β-C elim.) to **II** because rapid β-hydride elimination (β-H elim.) from **II** would prevent the formation of **4a** due to the presence of a reactive allylic C–H bond. Finally, **3a** was predominantly produced as a sole HCN adduct through **V**. Because **II** could release a H–Ni species



Scheme 7. Plausible reaction pathway.

through β-H elimination, perfect D-incorporation in H_A was not observed even when a large excess of DCN was used, as shown in Scheme 5.

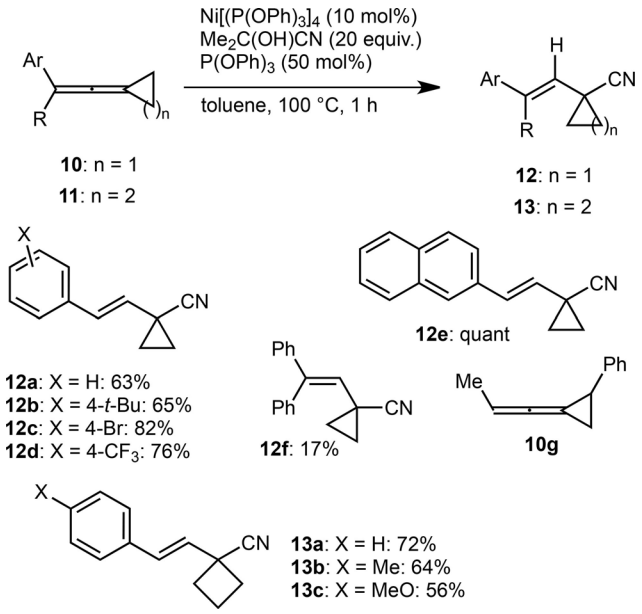
To study the reactivity of the α-cyclopropyl Ni species (**I**), we next investigated the Ni-catalyzed hydrocyanation of methylenecyclopropanes (Scheme 8).[20]



Scheme 8. Hydrocyanation of **6**.

Although two modes of C–H bond formation to **6** could be proposed, **7** was obtained as a sole product. A C–Ni bond at a benzylic position in **VI** could be predominantly formed and subsequent cyclopropane cleavage would give **VII**, which gives **7** through **9** *via* a β-H elimination–hydrocyanation sequence. The substrate scope clearly shows good agreement with the above proposed mechanism without the observation of a primary carbonitrile (**8**) or conjugated dienes (**9**). For example, **7a** was exclusively obtained from **6a** in 63% yield and its stereochemistry was assigned to be *trans*. Bromo, *tert*-butyl and CF_3 functionalities as well as β-naphthyl and 2-thiophene gave **7b–g** in yields of 67–93%. In cases of **6h** and **6i**, the reaction did not proceeded due to the lower reactivity of the C=C double bonds.[21]

Furthermore, we investigated vinylidenecyclopropanes (**10**), which have features of both allenes and methylenecyclopropanes (Scheme 9). The reaction of **10a** exclusively gave **12a** without the cleavage of any cyclopropanes, which suggests that **10** has an "allenyl character" to form a C–H bond at the *sp* carbon to

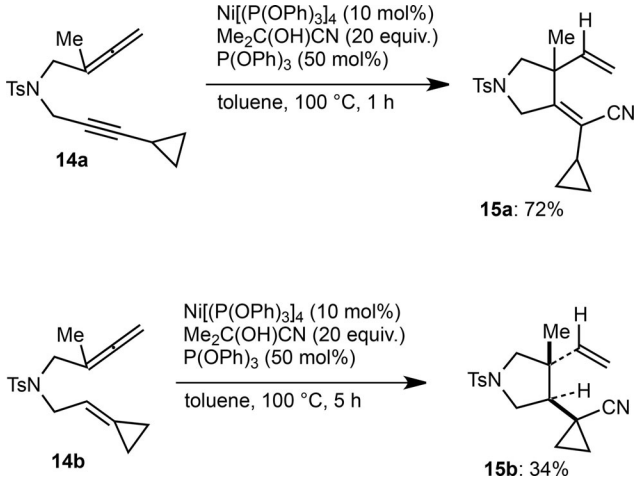


Scheme 9. Hydrocyanation of **10** and **11**.

give allyl Ni(II) intermediates. In addition, a cyano group could be selectively installed on a cyclopropane ring to maintain conjugation, as observed in arylallenes.[18] Other substrates (**10b–e**) gave the corresponding adducts in 65% to quantitative yields. Ever a tetra-substituted allene such as **10f** (R = Ar = Ph) gave **12f** in 17% yield, which indicates that vinylidenecyclopropane (**10f**) is more reactive than alkylidenecyclopropane (**6i**). When the reaction of **10g**, which has a methyl substituent on the allene, was examined, none of the desired adducts were obtained at all. In the case of a cyclobutane system, the reaction also proceeded smoothly to give the corresponding adducts **13a–c**. The results shown above suggest that the initial hydronickelation is strongly influenced by the nature of the C=C double bonds and substituents, and allenyl C=C double bonds are the most reactive in hydronickelation.

To confirm the reactivity described above, allene-yne and allene-ene systems bearing cyclopropanes were next investigated and found to give a single product triggered by hydronickelation at the *sp* carbon of the allene (Scheme 10). The reaction of **14a** gave **15a** as a single diastereomer in 72% yield. Its structure revealed that the initial C–H bond formation favorably occurred at an *sp* carbon on the allene, as observed in our previous studies.[8b–d,18] When a C≡C triple bond was replaced by methylenecyclopropanes, **14b** required a longer reaction time to cyclize and **15b** was exclusively obtained in 34% yield without any ring cleavage. The stereochemistry of **15b** was assigned based on NOESY correlations between the methyl and cyclopropyl methylene protons.

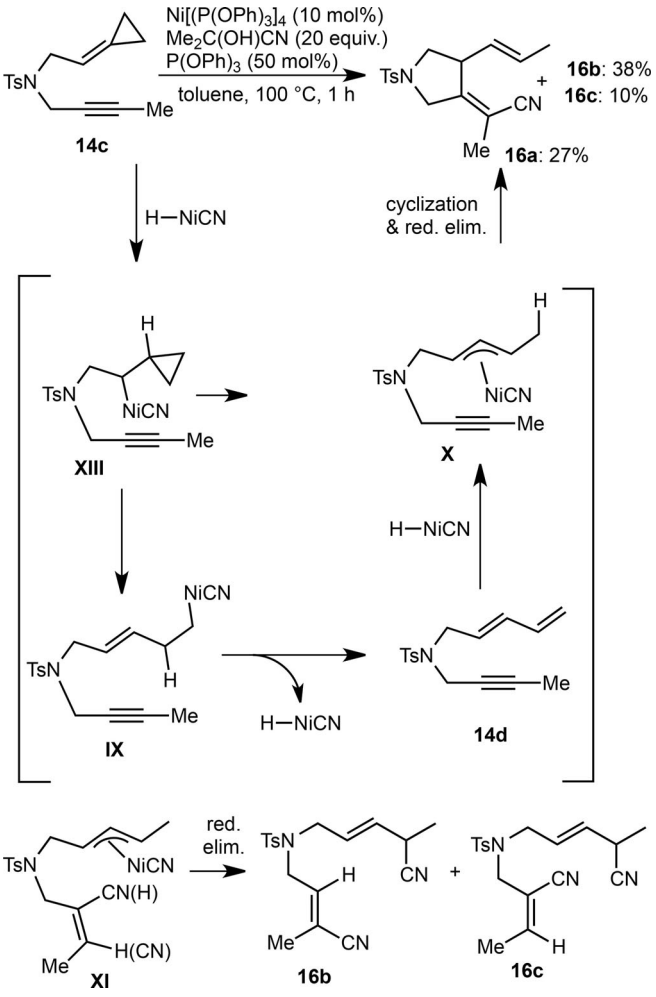
On the other hand, a substrate having both a methylenecyclopropane and a triple bond such as **14c** gave



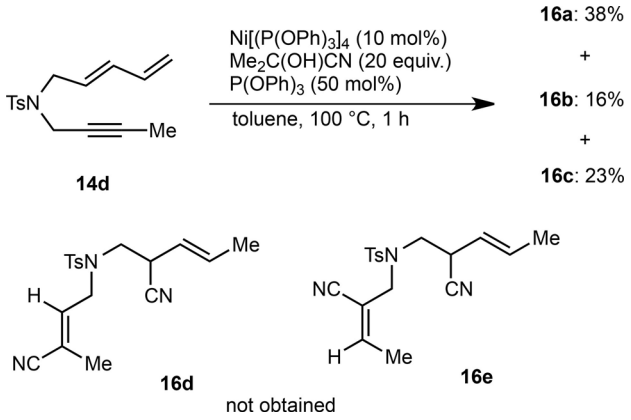
Scheme 10. Hydrocyanative cyclization of **14a** and **14b**.

16a–c through the cleavage of the cyclopropane (Scheme 11). The trigger to give the cyclization product (**16a**) would be hydronickelation to methylenecyclopropane (**XIII**). Subsequent cleavage of cyclopropane gives diene (**14d**) through **IX**. The second hydronickelation gives **X**, which would cyclize to **16a** in 27% yield. Non-cyclized products (**16b** and **16c**) could be produced in respective yields of 38% and 10% by an initial hydronickelation to a triple bond of **14c** followed by a second hydronickelation, which would promote cyclopropane cleavage through **XI**. This result suggests that the alkyne would be more reactive than the methylenecyclopropane.

The similar results obtained with **14d** contribute strong evidence to support the above plausible pathway (Scheme 12). A conjugated diene is a suitable



Scheme 11. Hydrocyanation of **14c** and mechanistic proposal.



Scheme 12. Hydrocyanation of **14d**.

functionality for regioselective hydrocyanation, and 5-*exo* cyclization from **X** would give **16a** in 38% yield.[8a,b] Other products (**16b** and **16c**) would result from the double hydrocyanation to a C≡C triple bond followed by a conjugated diene. The similar yields of **16a** and **16b** and **16c** indicate that a conjugated diene and an alkyne had similar reactivities. Isomeric products such as **16d** and **16e** were not obtained at all.

Conclusions

We have demonstrated the regio- and stereoselective hydrocyanation of allenes through the regioselective cleavage of cyclopropanes under nickel catalysis. The reaction pathway could be determined by the initial hydronickelation and finally gives a sole HCN adduct *via* regioselective C–CN bond formation. These findings revealed that simple allenes are much more reactive than alkynes, conjugated dienes, methylenecyclopropanes and vinylidenecyclopropanes (reactivity order: allene ≫ alkyne = conjugated diene > methylenecyclopropane), and these are important findings in the design of a new reaction of hydronickelation.

Experimental Section

General Procedure for the Hydrocyanative Cyclization; Synthesis of 15a

A solution of **14a** (0.12 mmol), $P(OPh)_3$ (15.9 μL, 0.06 mmol), $Ni[P(OPh)_3]_4$ (0.012 mmol, 15.8 mg) and acetone cyanohydrin (0.22 mL, 2.42 mmol) in toluene (0.12 mL) was heated at 100 °C for 1 h under an argon atmosphere. The reaction mixture was poured onto silica gel to be purified by column chromatography (*n*-hexane/AcOEt = 15/1) to give **15a** as colorless solid; yield: 29.7 mg (72%); mp 97–100 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.71–0.77 (m, 2H), 0.83–0.89 (m, 2H), 1.23–1.30 (m, 1H), 1.45 (s, 3H), 2.46 (s, 3H), 3.08 (d, 1H, *J* = 9.6 Hz), 3.15 (d, 1H, *J* = 9.6 Hz), 3.95 (d, 1H, *J* = 16.0 Hz), 4.09 (d, 1H, *J* = 16.0 Hz), 5.19 (d, 1H, *J* = 17.2 Hz), 5.21 (d, 1H, *J* = 10.4 Hz), 5.78 (dd, 1H, *J* = 17.2, 10.4 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 7.71 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 6.3, 6.4, 7.8, 12.2, 21.6, 49.1, 52.2, 60.4, 110.4, 113.9, 115.8, 128.0, 129.9, 131.5, 138.4, 144.3, 157.9; IR (ATR) ν: 2929, 2215, 1597, 1486, 1347, 1161 cm^{-1}; HR-MS (ESI): *m/z* = 365.1317, calcd. for $C_{19}H_{22}N_2NaO_2S$ $[M+Na]^+$: 365.1300.

Acknowledgements

The authors are grateful for financial support from KAKENHI (21590003 for S.A. and 15J04214 for H.H.), the Uehara Memorial Foundation (S.A.) and The Naito Foundation (S.A.).

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