CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200700028

Highly Efficient Synthesis of Stereodefined Multisubstituted 1,4-Dicyano- and 1-Cyano-1,3-butadienes and Their Reactions with Organolithium Reagents

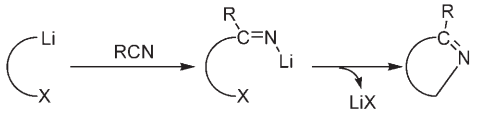
Congyang Wang,[a] Chao Wang,[a] Qifeng Wang,[b] Zhihui Wang,[a] Hui Sun,[a] Xiangyu Guo,[a] and Zhenfeng Xi*[a, c]

Abstract: Stereodefined multisubstituted 1-cyano- and 1,4-dicyano-1,3-butadiene derivatives were obtained in excellent yields of the isolated product from their corresponding monohalo- and dihalobutadienes and CuCN. This reaction proceeded with high stereoselectivity and retention of the stereochemistry of the starting halobutadienes. A study of the utility of the thus-obtained 1-cyano- and 1,4-dicyano-1,3-butadiene derivatives was demonstrated by their reactions with organolithium reagents. 2*H*-Pyrrole or iminocyclopentadiene derivatives were formed in high yields from 1-cyano-4-halo-1,3-butadienes and organolithium reagents. When 1,4-dicyano-1,3-butadienes were treated with organolithium reagents followed by trapping with electrophiles, a tandem process took place to afford 2*H*-pyrrolyl nitriles in excellent yields. Reduction of 1,4-dicyano-1,3-butadiene derivatives with $LiAlH_4$ showed novel reaction patterns relative to normal nitriles.

Keywords: butadienes · lithiation · nitriles · stereoselectivity · synthetic methods

Introduction

The addition reaction of organolithium reagents to organonitriles provides an important synthetic protocol.[1–4] As a conventional pathway,[3,4] the addition reaction intermediates, *N*-lithioketimines, when generated in situ are intramolecularly trapped by an organohalide moiety positioned at the other end of the molecule through nucleophilic substitution to generate nitrogen-containing heterocycles, such as pyridines (Scheme 1).[5,6] We have recently reported reactions of 1,4-dilithio- and 1-lithio-1,3-butadienes **1** with organonitriles that afford pyridines **2** and/or pyrroles **3** through an unprecedented cycloaddition reaction (Scheme 2).[7,8] In our unusual cycloaddition reaction without a nucleophilic substitution step, *N*-lithioketimine **4** was proposed to be the key intermediate (Scheme 2).[7,8]



Scheme 1. The conventional way to nitrogen-containing heterocycles from *N*-lithioketimines generated from organolithium reagents and nitriles.

To extend the scope of these synthetically useful reactions and to further investigate the reaction mechanisms, we planned to treat 1-cyano-1,3-dienes **7** and **8** and 1,4-dicyano-1,3-dienes **9** with various organolithium reagents (Scheme 3). We expected these reactions to lead to the formation of a

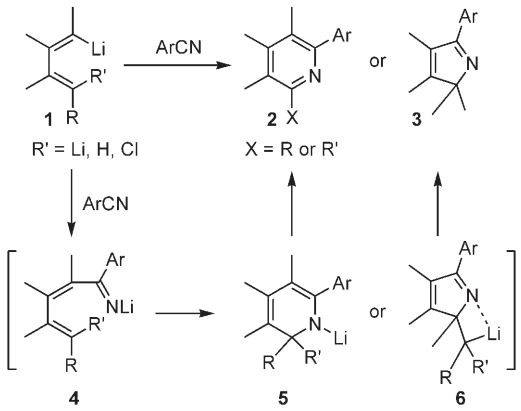
[a] Dr. C. Y. Wang, C. Wang, Dr. Z. Wang, H. Sun, X. Guo, Prof. Dr. Z. Xi
Beijing National Laboratory for Molecular Sciences (BNLMS)
Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education
College of Chemistry, Peking University, Beijing 100871 (China)
Fax: (+86) 10-6275-1708
E-mail: zfxi@pku.edu.cn

[b] Q. Wang
Institute of Chemistry
Chinese Academy of Sciences
Beijing 100080 (China)

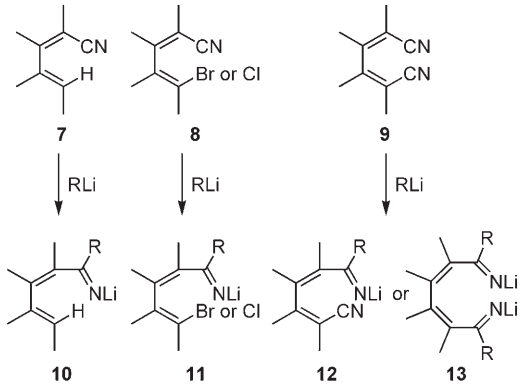
[c] Prof. Dr. Z. Xi
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences, Shanghai 200032 (China)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

WILEY InterScience DISCOVER SOMETHING GREAT
© 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 2. Reaction of 1,4-dilithio- and 1-lithio-1,3-dienes with organonitriles.



Scheme 3. Expected reactions of 1,4-dicyano- and 1-cyano-1,3-dienes with organolithium reagents.

wide variety of *N*-lithioketimines, such as **10**–**13**, which might lead to structurally important products, including pyridines **2** and pyrroles **3**, upon further manipulation.

However, ironically, we found that, although α,β-unsaturated nitriles are versatile intermediates in organic synthesis and can invoke various functional group transformations and be used to construct useful carbocycles or heterocycles,[9–11] no general synthetic method for 1,4-dicyano- or 1-cyano-1,3-diene derivatives has been reported. In fact, for the preparation of alkenyl nitriles, especially for aryl nitriles, there are several methods, including the Horner–Wadsworth–Emmons olefination of carbonyl compounds with α-cyano phosphonates,[12] the synthesis of dienenitriles by the 1,4-addition of organocopper and alkyl argintate reagents to enynenitriles,[13] and the substitution of alkenyl or aryl halides using CuCN.[14,15] After applying and modifying several known procedures, we found that the substitution of the halogen atom using CuCN was the best choice for our target multisubstituted monocyano- and dicyanobutadienes. Thus, a synthetically useful method for the preparation of 1,4-dicyano- and 1-cyano-1,3-dienes of diverse structures and substitution patterns was first developed. With ready access to a variety of multisubstituted 1,4-dicyano- or 1-cyano-1,3-diene derivatives, we investigated reactions of these cyanodienes with organolithium reagents as a demonstration of such useful and important molecules. Their reaction with organolithium reagents did show unique properties. We expect these multisubstituted 1,4-dicyano- or 1-cyano-1,3-diene derivatives will be widely applicable in organic synthesis and in the synthesis of organomaterials.

Results and Discussion

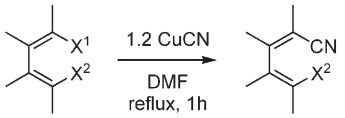
Synthesis of stereodefined multisubstituted 1-cyano-1,3-butadiene and 1,4-dicyano-1,3-butadiene derivatives: 1-Halo- and 1,4-dihalo-1,3-butadienes can be readily obtained in excellent yields by the halogenation of metallacyclopentadienes.[16,17] When diene halide **14** was treated with 1.2 equivalents of CuCN in *N*,*N*-dimethylformamide (DMF) at reflux over one hour, the dienenitrile **7** was obtained in excellent yield of the isolated product and with perfect stereoselectivity (representative examples are given in Table 1). Both iododienes and bromodienes could be used in this type of reaction. The vinyl chloride moiety was inert under the reaction conditions and 4-chlorodienenitrile **8a**,**b** was formed as the sole product in 94 and 91% yield of the isolated product, respectively (Table 1, entries 7 and 8).

1,4-Dicyano-1,3-butadienes could be also obtained following the same method. When diiodide **15** was treated with 2.4 equivalents of CuCN for a prolonged reaction time, the dienedinitrile **9** was obtained in excellent yield and with perfect stereoselectivity (representative results are shown in Table 2). Both symmetrical and unsymmetrical dienedinitriles can be obtained (Table 2, entries 1–3). Dienedihalides with an aliphatic cycle or with one aryl iodide moiety both led to the corresponding dienedinitriles **9d**–**f** in excellent yield of the isolated products (Table 2, entries 4–6). Tri- or disubstituted dienedinitriles could be also prepared from their corresponding diiodides in excellent yields (Table 2, entries 7–10). It is noteworthy that no isomerization of the C=C bonds was observed in all cases. This result is in contrast to the reported isomerization problem for alkenyl halides. For example, Procházka et al. reported that (*Z*)-1-bromo-1-propene when treated with CuCN in DMF gave (*E*)- and (*Z*)-2-butenenitrile in 60 and 27% yield, respectively.[14a] In our case, the butadienyl halides underwent the coupling reaction with retention of stereoselectivity.

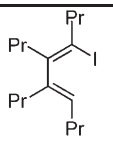
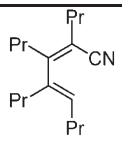
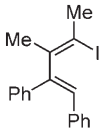
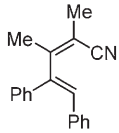
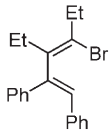
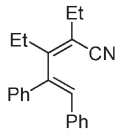
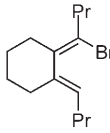
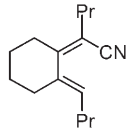
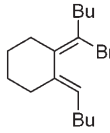
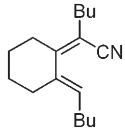
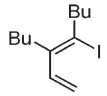
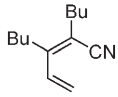
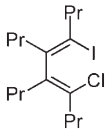
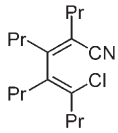
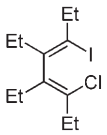
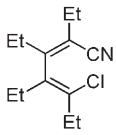
When 1,4-dibromo-1,3-diene **16** was used as the starting material, a mixture of monocyano- and dicyanodienes were formed as the products. Neither largely excessive amounts of CuCN nor prolonged reaction times could be used to obtain the dienedinitrile as the sole product. On the other hand, many attempts were carried out to stop the reaction at the first cyanation step to afford 4-bromodienenitrile **8c**, which is also very useful for preparing further functionalized dienenitriles. The amount of CuCN was found to be crucial for the reaction selectivity. Finally, dibromodiene **16** was transferred into the 4-bromodienenitrile **8c** in 62% yield of

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 1. Preparation of 1-cyano-1,3-dienes from 1-halodienes and CuCN.

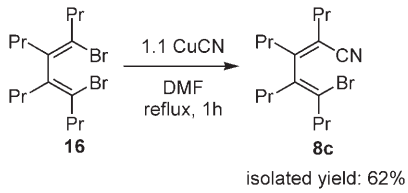


14 **7**: X^2 = H
X^1 = Br, I X^2 = H, Cl **8**: X^2 = Cl or Br

Entry	Dienehalide **14**	Dienenitrile **7, 8**		Yield [%][a]
1			**7a**	94
2			**7b**	85
3			**7c**	82
4			**7d**	96
5			**7e**	90
6			**7f**	98
7			**8a**	94
8			**8b**	91

[a] Yield of the isolated product.

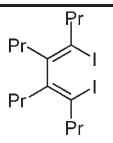
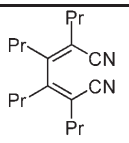
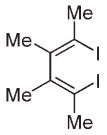
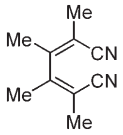
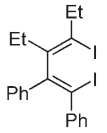
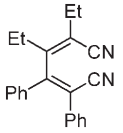
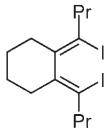
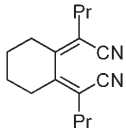
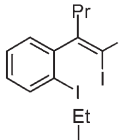
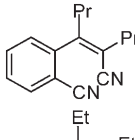
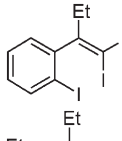
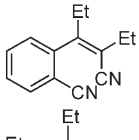
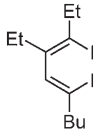
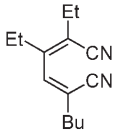
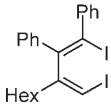
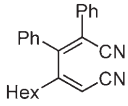
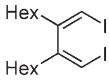
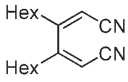
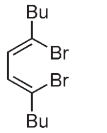
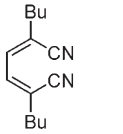
the isolated product with 1.1 equivalents of CuCN in DMF at reflux for one hour (Scheme 4).



Scheme 4. Synthesis of monocyano monobromobutadiene **8c**.

Table 2. Preparation of 1,4-dicyano-1,3-dienes from 1,4-dihalo- 1,3-dienes and CuCN.

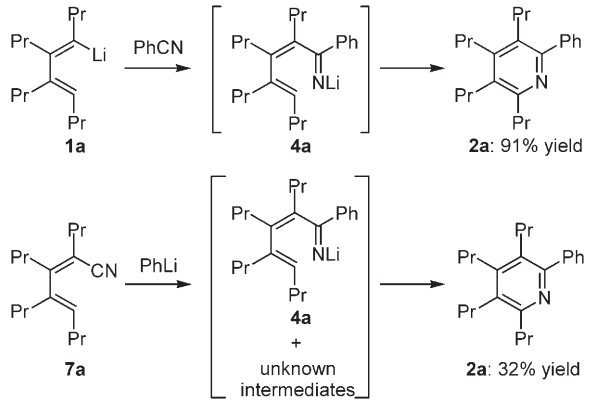
15 **9**

Entry	Dihalodiene **15**	Dicyanodiene **9**		Yield [%][a]
1			**9a**	95
2			**9b**	90
3			**9c**	96
4			**9d**	93
5			**9e**	93
6			**9f**	94
7			**9g**	97
8			**9h**	98
9			**9i**	81
10			**9j**	90

[a] Yield of the isolated product.

Reactions of multisubstituted 1-cyano-1,3-diene derivatives with organolithium reagents: As mentioned above, we previously proposed that pyridine derivatives are formed through the intramolecular cycloaddition of *N*-lithioketimines **4** that are generated in situ from 1-lithio-1,3-diene derivatives **1** and organonitriles (Scheme 2).[3,7,8,18,19] As shown in Scheme 5, the pyridine derivative **2a** was obtained in 91%

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim



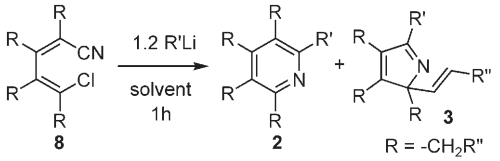
Scheme 5. Reaction of 1-cyano-1,3-butadiene with an organolithium reagent relative to the reaction of 1-lithio-1,3-butadiene with an organonitrile.

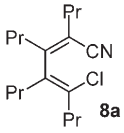
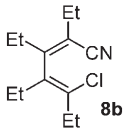
yield of the isolated product from the organolithium reagent **1a** and PhCN.[7,8] The same addition intermediate, *N*-lithioketimine **4a**, was assumed to be formed also in the reaction of 1-cyano-1,3-butadiene **7a** with PhLi. However, unfortunately, although the reaction of **7a** with PhLi proceeded smoothly, it afforded the pyridine derivative **2a** in a low yield (Scheme 5). In addition to **2a**, several unknown products were also formed in this reaction. The reason why these two reactions gave different results is not clear yet.

Surprisingly, when 4-chlorodienenitriles **8a** and **8b** were treated with organolithium reagents in THF at reflux, the five-membered nitrogen-containing heterocycles 2*H*-pyrroles **3** were obtained in high yields (representative results are given in Table 3). It is noteworthy that only the *E* isomers of alkenyl 2*H*-pyrroles **3** were observed, thus indicating that the reaction proceeded with excellent stereoselectivity. Interestingly, bulky *t*BuLi can also undergo a similar process, thus smoothly leading to **3b** in 91% yield of the isolated product (Table 3, entry 2). The solvent was found to be very important for this reaction. When the reaction was carried out in diethyl ether, pyridine derivatives **2** were formed in addition to products **3** (Table 3, entries 6–8). For example, the reaction of **8a** with *n*BuLi in THF afforded **3a** as the sole product in 90% yield of the isolated product (Table 3, entry 1), whereas the same reaction in diethyl ether afforded a mixture of two products **2b** and **3a** in 16 and 71% yields of the isolated products, respectively (Table 3, entry 7). The reaction of **8b** with PhLi gave **3e** in 86% yield of the isolated product with a trace amount of **2e** in THF (Table 3, entry 5). However, **2e** became the major product in diethyl ether (Table 3, entry 6).

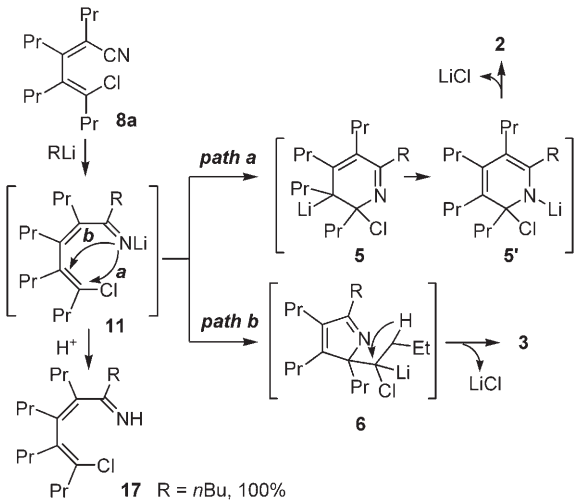
A proposed mechanism for the above reaction is given in Scheme 6. The nucleophilic addition may take place firstly to form the *N*-lithioketimines **11**. Indeed, when the reaction was carried out at −50 °C for one hour, quenching the reaction mixture did give the linear imine **17** as the sole product in a quantitative yield. In principle, two pathways can be considered for intermediate **11** to undergo anionic ring closure. One is the 6-*endo* addition of iminolithium species to

Table 3. Reactions of 4-chlorodienenitriles and organolithium reagents.



Entry	Dienenitrile **8**	R′Li	Solvent[a]	Yield **2** [%][b]		Yield **3** [%][b]	
1	 **8a**	*n*BuLi	THF	**2b**	0	**3a**	90
2	**8a**	*t*BuLi	THF	**2c**	0	**3b**	91
3	**8a**	MeLi	THF	**2d**	6	**3c**	78
4	**8a**	PhLi	THF	**2a**	7	**3d**	73
5	 **8b**	PhLi	THF	**2e**	trace	**3e**	86
6	**8b**	PhLi	Et_2O	**2e**	61	**3e**	18
7	**8a**	*n*BuLi	Et_2O	**2b**	16	**3a**	71
8	**8a**	PhLi	Et_2O	**2a**	61	**3d**	27

[a] THF: at reflux; Et_2O: room temperature. [b] Yield of the isolated product.



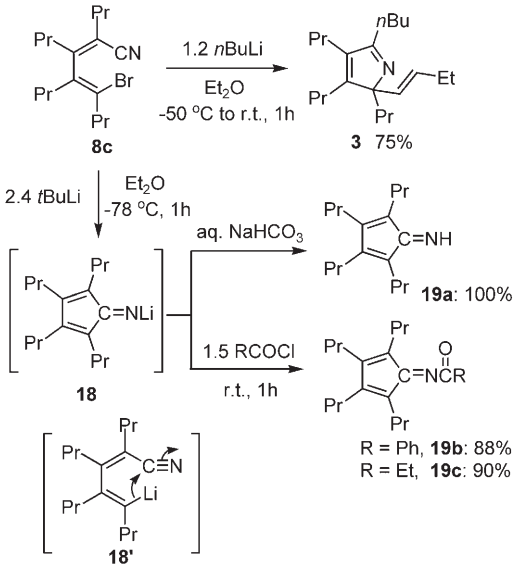
Scheme 6. Proposed mechanism for the reaction of 4-chlorodienenitriles and an organolithium reagent.

the C=C double bond to give the intermediates **5** and **5′**, which subsequently afforded pyridine product **2** through elimination of LiCl (Scheme 6, path a). The other is the 5-*exo* addition of the iminolithium species to the C=C bond to form the intermediate **6** followed by elimination of LiCl and hydrogen transfer to afford the final 2*H*-pyrrole product **3** (Scheme 6, path b).[8]

When 4-bromodienenitrile **8c** was treated with *n*BuLi, 2*H*-pyrrole **3a** was obtained in 75% yield of the isolated product through a similar process to that described above.

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

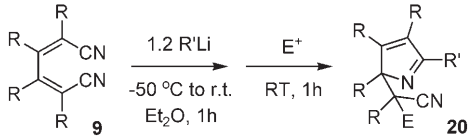
Nevertheless, when treated with *t*BuLi, iminocyclopentadiene **19a** was obtained in a quantitative yield upon quenching with aqueous $NaHCO_3$ (Scheme 7). Neither pyridine **2** nor 2*H*-pyrrole **3**, which should arise from the addition of an organolithium reagent to a nitrile, was observed. The use of acid chlorides to trap the reaction intermediate afforded acylimine **19b,c** in 88 and 90% yield of the isolated products, respectively. In these cases, a bromine–lithium exchange was proposed to take place first to afford the intermediate **18′**, which underwent intramolecular attack on the cyano group of the vinyl lithium reagent generated in situ, thus giving the cyclic *N*-lithioketimine intermediate **18**. Further functionalized products, such as **19**, can be formed by the ready trapping of intermediate **18** by electrophiles.

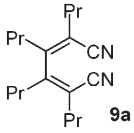
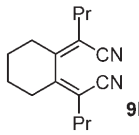
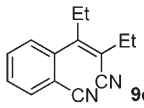


Scheme 7. Reaction of 4-bromodienenitrile **8c** with an organolithium reagent.

Reactions of multisubstituted 1,4-dicyano-1,3-diene derivatives with organolithium reagents: Although reactions of 1,4-dicyanobutadiene with transition-metal complexes have been investigated in several cases,[20,11c–d] the reactivity of dienedinitriles with main-group-metal compounds has seldom been explored. We found dienedinitriles **9** reacted with organolithium reagents followed by quenching with aqueous $NaHCO_3$ to give 2*H*-pyrrolyl nitrile derivatives **20** in excellent yield with d.r. values of about 3:2 in all cases, and none of expected diimine products were observed (representative results are given in Table 4). Dienedinitriles with an aliphatic cycle **9b** or with one aryl nitrile moiety **9c** both led to the final products in high yields (Table 4, entries 6–9). Both aliphatic and aromatic organolithium reagents can be applied to this reaction. Trapping the reaction mixture with carbon electrophiles afforded the alkylated 2*H*-pyrrolyl nitrile derivative **20b,c** solely (Table 4, entries 2 and 3).

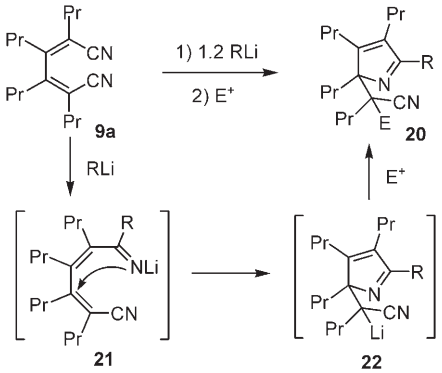
Table 4. Reaction of dienedinitriles **9** with organolithium reagents.



Entry	Dienedinitrile **9**	R′Li	Electrophile	Yield [%][a]
1	 **9a**	*n*BuLi	H^+	**20a** 100
2	**9a**	*n*BuLi		**20b** 100
3	**9a**	*n*BuLi	$PhCH_2Br$	**20c** 90
4	**9a**	PhLi	H^+	**20d** 93
5	**9a**	MeLi	H^+	**20e** 95
6	 **9b**	*n*BuLi	H^+	**20f** 88
7	**9b**	PhLi	H^+	**20g** 75
8	 **9c**	*n*BuLi	H^+	**20h** 85[b]
9	**9c**	PhLi	H^+	**20i** 75[b]

[a] Yield of the isolated product; d.r. = 3:2 [b] Solvent: THF.

A proposed mechanism for the above reactions is shown in Scheme 8. Nucleophilic addition of an organolithium reagent to one of the two cyano groups must take place as the first step to form *N*-lithioketimine intermediate **21**, which underwent an intramolecular Michael addition to give the 2*H*-pyrrolyl lithium intermediate **22**. Trapping the intermediate **22** with electrophiles afforded the product **20** eventually. Thus, the 2*H*-pyrrolyl nitrile derivatives **20** can be readily constructed through this tandem process in one pot.

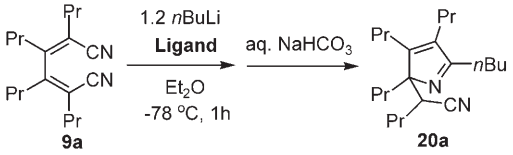


Scheme 8. Proposed mechanism for reaction of dienedinitrile **9** with an organolithium reagent.

Interestingly, better stereoselectivity was observed on the addition of ligands to the reaction mixture (Table 5). For example, when dienedinitrile **9a** was treated with *n*BuLi in the

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Table 5. Ligand's effect on reaction of dienedinitrile **9a** with *n*BuLi.



Ligand	Yield [%][a]	d.r.[b]
none	66	59:41
TMEDA[c]	76	76:24
sparteine[c]	96	83:17
sparteine[d]	71	75:25

[a] Yield of the isolated product. [b] Detected by HPLC. [c] 1.0 equivalents. [d] 0.1 equivalents.

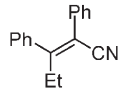
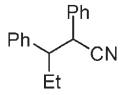
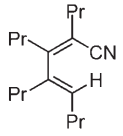
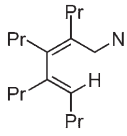
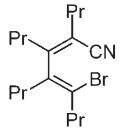
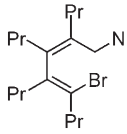
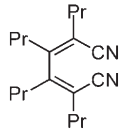
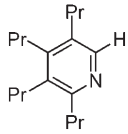
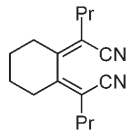
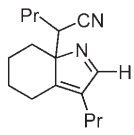
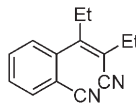
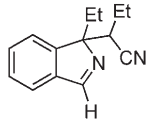
absence of a ligand, d.r. = 59:41 for the final product **20a**. When the reaction was carried out with 1.0 equivalents of TMEDA, the diastereoisomeric ratio increased to 76:24. In the presence of 1.0 equivalents of sparteine, the reaction was completed at −78 °C within one hour and d.r. = 83:17, which showed an obvious increase both in the reactivity and stereoselectivity. Furthermore, the product was obtained in 71 % yield of the isolated product and d.r. = 75:25, even with 0.1 equivalents of sparteine.

Reduction of 1,4-dicyano- and 1-cyano-1,3-diene derivatives with lithium aluminum hydride: The reduction of organonitriles has been a fundamental synthetic method in organic synthesis. However, when both a C≡N bond and another unsaturated chemical bond, such as the C=C bond, exist in the same molecule, selective reduction of the unsaturated bonds is desired.[21,22] Simple nitrile groups are known to be reduced to primary amines by $LiAlH_4$.[21] In the case of α,β-unsaturated nitriles, both reduction of the C≡N and C=C bonds are reported in different substrates.[22] When we treated unsaturated nitriles **23** with 1.0 equivalents of $LiAlH_4$ in diethyl ether, the C=C bond was selectively reduced to give **24** in 89 % yield of the isolated product (Table 6, entry 1). However, on the contrary, treatment of dienenitrile **7a** with 1.0 equivalents of $LiAlH_4$ afforded the primary amine **25a** as the sole product in 85 % yield of the isolated product (Table 6, entry 2). This selectivity is in sharp contrast to the result obtained with α,β-unsaturated nitrile **23**. In a similar manner, 4-bromodienenitrile **8c** was reduced to its corresponding amine **25b**, and no product with a reduced C=C bond was observed (Table 6, entry 3).

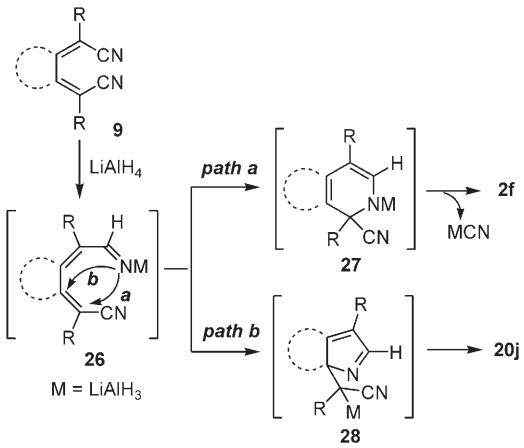
Very interestingly, the reaction of dienedinitriles **9a** with 1.0 equivalents of $LiAlH_4$ afforded a cyclic product, the pyridine derivative **2f**, in 75 % yield of the isolated product (Table 6, entry 4). Furthermore, different types of cyclic products other than the above-described pyridine derivatives, such as the 2*H*-pyrrole derivatives **20j** and **20k**, were obtained, respectively, from the reaction of **9d** and **9f** with 1.0 equivalents of $LiAlH_4$.

A proposed reaction mechanism for the above-described novel reduction–cyclization process is shown in Scheme 9.

Table 6. Reaction of different conjugated enenitriles with $LiAlH_4$.

Entry	Substrate		*T* [°C]	Product		Yield [%][a]
1		**23**	0		**24**	89[b]
2		**7a**	30		**25a**	85
3		**8c**	30		**25b**	80
4		**9a**	−30		**2f**	75
5		**9d**	−30		**20j**	65[c]
6		**9f**	−30		**20k**	51[c]

[a] Yield of the isolated product; solvent: Et_2O, 1 h. [b] Two isomers: d.r. = 3:1. [c] Two isomers: d.r. = 1:1.



Scheme 9. Proposed mechanism for the reaction of dienedinitrile **9** with $LiAlH_4$.

The reduction of the C≡N bond into an imino anion is assumed to be the first step in the formatin of intermediate **26**. This linear intermediate **26** may then undergo 6-*endo* intramolecular addition to form the cyclic intermediate **27** (Scheme 9, path a). Elimination of MCN finally afforded the pyridine product **2f**.[23] On the contrary, when dienedinitrile **9d** was treated with 1.0 equivalents of $LiAlH_4$ (Table 6, entry 5), the 2*H*-pyrrole derivative **20j**, which is obtained

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

from the 5-*exo* addition of the imino anion generated in situ, was obtained as the major product (Scheme 9, path b). Although the reason for such regioselectivity is not yet clear, the conformation of the cyclic dienedinitrile **9d** may play an important role in the reaction. In the case of dienedinitrile **9f**, the 2*H*-pyrrole derivative **20k** was obtained as the major product in moderate yield (Table 6, entry 6). The dearomatization step in the formation of pyridine is unfavorable, which is considered to be the main reason for the selectivity in the formation of 2*H*-pyrrole derivative **20k**.

Conclusion

In conclusion, we have realized a practical synthesis of 1-cyano- and 1,4-dicyano-1,3-dienes from readily available starting materials and CuCN in yields of 81–98% and with excellent stereoselectivities. This method provides rapid access to multisubstituted, stereodefined dienenitrile/dinitriles, which are expected to have wide applications in synthetic chemistry and the field of organomaterials. The utility of these unsaturated nitriles in organic synthesis is demonstrated by their reactions with organolithium reagents. 2*H*-Pyrrole or iminocyclopentadiene derivatives were formed in good-to-excellent yields from 4-halodienenitriles and organolithium reagents. 2*H*-Pyrrolyl nitrile derivatives are readily constructed from dienedinitriles and organolithium reagents in high yields through tandem processes in one pot. The reduction of these unsaturated nitriles with $LiAlH_4$ afforded amine, pyridine, or pyrrole derivatives, in which unprecedented reaction patterns relative to normal nitriles were observed. Further exploration of the reactivity of dienenitrile/dinitriles as useful building blocks in synthetic chemistry is being carried out in our group.

Experimental Section

General: The nucleophilic substitution reactions of butadiene halides with cuprous cyanide were carried out in air. The reactions of butadienedinitrile with organolithium reagents were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Diethyl ether was heated to reflux and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. All the organolithium reagents were obtained from Acros Organics.

^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in $CDCl_3$ (containing 0.1% tetramethylsilane (TMS)) on a JEOL JNM-AL300 NMR spectrometer. All the butadiene halides were synthesized by a previously reported procedure.[24]

A typical procedure for the preparation of 1-cyano-1,3-buatadienes 7a–f and 8a,b from their corresponding 1-halo-1,3-butadienes: CuCN (1.2 mmol) was added to a solution of 1-halo-1,3-butadiene (1.0 mmol) in DMF (5 mL) at room temperature. The reaction mixture was heated to reflux and stirred for 1 h to generate 1-cyano-1,3-butadiene, the formation of which was monitored by GC analysis or TLC. The reaction mixture was then filtered, and the solvent was evaporated in vacuo to give a black oil, which was purified by column chromatography (silica gel, Et_2O/hexane 1:30) to afford **7a–g** and **8a,b**.

Dienenitrile 7a: Colorless liquid obtained in 94% yield of the isolated product (232 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.86$–0.98 (m, 12H), 1.28–1.66 (m, 8H), 2.07–2.25 (m, 8H), 5.48 ppm (t, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.47$, 13.88, 13.94, 14.22, 21.14, 21.77 (2 CH_2), 22.54, 30.11, 30.73, 31.99, 110.37, 120.16, 132.35, 139.37, 161.85 ppm; HRMS calcd for $C_{17}H_{29}N$ 247.2300; found 247.2305.

Dienenitrile 7b: Colorless solid obtained in 85% yield of the isolated product (220 mg). M.p. 60–61 °C; ^{1}H NMR ($CDCl_3$, TMS): $\delta = 1.75$ (d, $J =$ 1.2 Hz, 3H), 2.02 (d, $J = 1.2$ Hz, 3H), 6.79 (s, 1H), 7.02–7.30 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 17.20$, 18.19, 105.67, 120.39, 127.43, 127.91, 127.94, 128.69, 129.44, 129.76, 130.95, 135.95, 137.32, 142.23, 156.67 ppm; HRMS calcd for $C_{19}H_{17}N$ 259.1361; found 259.1360.

Dienenitrile 7c: Colorless liquid obtained in 82% yield of the isolated product (235 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.95$ (t, $J = 7.5$ Hz, 3H), 1.25 (t, $J = 7.5$ Hz, 3H), 2.10 (q, $J = 7.5$ Hz, 2H), 2.37 (q, $J = 7.5$ Hz, 2H), 6.75 (s, 1H), 7.03–7.28 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta =$ 12.49, 13.25, 23.54, 23.69, 112.86, 119.63, 127.39, 127.89, 127.95, 128.67, 129.41, 129.77, 132.13, 136.11, 137.41, 140.92, 161.57 ppm; HRMS calcd for $C_{21}H_{21}N$ 287.1674; found 287.1673.

Dienenitrile 7d: Colorless liquid obtained in 96% yield of the isolated product (208 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.92$–0.97 (m, 6H), 1.39–1.71 (m, 8H), 2.06–2.33 (m, 8H), 5.65 ppm (t, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.37$, 13.85, 21.82, 22.43, 26.60, 27.02, 29.09, 29.75, 31.20, 31.95, 105.58, 120.29, 129.39, 138.16, 160.21 ppm; HRMS calcd for $C_{15}H_{23}N$ 217.1831; found 217.1831.

Dienenitrile 7e: Colorless liquid obtained in 90% yield of the isolated product (221 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.88$–0.96 (m, 6H), 1.29–1.67 (m, 12H), 2.08–2.31 (m, 8H), 5.64 ppm (t, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.87$, 13.97, 22.05, 22.38, 26.60, 27.02, 27.44, 29.04, 29.80, 30.72, 31.14, 31.36, 105.76, 120.32, 129.61, 137.92, 159.96 ppm; HRMS calcd for $C_{17}H_{27}N$ 245.2144; found 245.2142.

Dienenitrile 7f: Colorless liquid obtained in 98% yield of the isolated product (187 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.91$–0.97 (m, 6H), 1.32–1.62 (m, 8H), 2.27–2.37 (m, 4H), 5.38–5.56 (m, 2H), 6.86–6.95 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.84$ ($2CH_3$), 22.29, 22.98, 27.20, 29.88, 30.52, 31.23, 112.89, 118.79, 119.03, 135.33, 153.27 ppm; HRMS calcd for $C_{13}H_{21}N$ 191.1674; found 191.1672.

4-Chlorodienenitrile 8a: Colorless liquid obtained in 94% yield of the isolated product (264 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.93$–1.01 (m, 12H), 1.37–1.73 (m, 8H), 1.98–2.12 (m, 2H), 2.24–2.47 ppm (m, 6H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.38$, 13.52, 14.33, 14.58, 20.81, 20.85, 21.53, 21.62, 31.71, 33.56, 34.14, 37.06, 113.33, 119.41, 133.15, 135.73, 156.57 ppm; HRMS calcd for $C_{17}H_{28}N^{35}Cl$ 281.1910; found 281.1912.

4-Chlorodienenitrile 8b: Colorless liquid obtained in 91% yield of the isolated product (205 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 1.02$–1.08 (m, 6H), 1.16–1.22 (m, 6H), 2.06–2.51 ppm (m, 8H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 11.81$, 12.48, 12.85, 12.90, 23.13, 24.30, 25.01, 28.67, 114.35, 119.15, 134.37, 135.59, 156.67 ppm; HRMS calcd for $C_{13}H_{20}N^{35}Cl$ 225.1284; found 225.1286.

A typical procedure for the preparation of,4-dicyano-1,3-butadienes 9a–j from the corresponding 1,4-dihalo-1,3-butadienes: CuCN (2.4 mmol) was added to a solution of 1,4-dihalo-1,3-butadiene (1.0 mmol) in DMF (5 mL) at room temperature. The reaction mixture was heated to reflux and stirred for 6 h to generate 1,4-dicyano-1,3-butadiene, the formation of which was monitored by GC analysis or by TLC. The reaction mixture was then filtered, and the solvent was evaporated in vacuo to give a black oil, which was purified by column chromatography (silica gel, Et_2O/hexane 1:20) to afford **9a–j**.

Dienedinitrile 9a: Colorless liquid obtained in 95% yield of the isolated product (258 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.96$–1.03 (m, 12H), 1.42–1.49 (m, 4H), 1.61–1.73 (m, 4H), 2.29–2.33 ppm (m, 8H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.02$, 13.85, 20.59, 20.92, 31.47, 32.51, 114.27, 118.09, 155.70 ppm; HRMS calcd for $C_{18}H_{28}N_2$ 272.2253; found 272.2255.

Dienedinitrile 9b: Colorless solid obtained in 90% yield of the isolated product (144 mg). M.p. 49–50 °C; ^{1}H NMR ($CDCl_3$, TMS): $\delta = 1.97$ ppm (s, 12H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 16.35$, 17.32, 107.30, 118.50, 154.13 ppm; HRMS calcd for $C_{10}H_{12}N_2$ 160.1001; found 160.1000.

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Dienedinitrile 9c: Colorless solid obtained in 96% yield of the isolated product (300 mg). M.p. 105–106 °C; ^{1}H NMR ($CDCl_3$, TMS): $\delta = 1.07$–1.12 (m, 3H), 1.31–1.36 (m, 3H), 2.26 (br, 2H), 2.46–2.54 (m, 2H), 7.06–7.31 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 12.06$, 12.53, 23.65, 24.28, 115.87, 117.28, 118.39, 118.54, 128.64 (2CH), 128.78 (2CH), 129.03, 129.38 (2CH), 129.65, 129.80 (2CH), 133.15, 134.41, 154.83, 156.72 ppm; HRMS calcd for $C_{22}H_{20}N_2$ 312.1627; found 312.1617.

Dienedinitrile 9d: Colorless liquid obtained in 93% yield of the isolated product (225 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 1.00$ (t, $J = 7.5$ Hz, 6H), 1.50–1.71 (m, 6H), 1.93–2.11 (m, 4H), 2.23–2.39 (m, 4H), 2.83–2.88 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.39$, 21.51, 27.41, 31.91, 32.01, 111.07, 118.38, 155.48 ppm; HRMS calcd for $C_{16}H_{22}N_2$ 242.1783; found 242.1778.

Dienedinitrile 9e: Colorless liquid obtained in 93% yield of the isolated product (221 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.93$ (t, $J = 7.2$ Hz, 3H), 1.06 (t, $J = 7.2$ Hz, 3H), 1.29–1.42 (m, 2H), 1.63–1.78 (m, 2H), 2.42 (t, $J = 7.5$ Hz, 2H), 2.57 (t, $J = 7.5$ Hz, 2H), 7.29–7.32 (m, 1H), 7.43–7.49 (m, 1H), 7.60–7.65 (m, 1H), 7.71–7.73 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.45$, 13.98, 20.79, 21.56, 32.05, 35.73, 111.65, 116.01, 117.43, 118.09, 128.80, 129.06, 132.90, 133.25, 144.32, 155.13 ppm; HRMS calcd for $C_{16}H_{18}N_2$ 238.1470; found 238.1474.

Dienedinitrile 9f: Colorless liquid obtained in 94% yield of the isolated product (197 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.98$ (t, $J = 7.5$ Hz, 3H), 1.27 (t, $J = 7.5$ Hz, 3H), 2.46 (q, $J = 7.5$ Hz, 2H), 2.61 (q, $J = 7.5$ Hz, 2H), 7.30–7.33 (m, 1H), 7.44–7.49 (m, 1H), 7.61–7.73 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 11.93$, 12.90, 23.53, 26.91, 111.73, 116.82, 117.34, 117.94, 128.86, 129.04, 132.96, 133.14, 143.87, 155.73 ppm; HRMS calcd for $C_{14}H_{14}N_2$ 210.1157; found 210.1157.

Dienedinitrile 9g: Colorless liquid obtained in 97% yield of isolated product (210 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.95$ (t, $J = 7.2$ Hz, 3H), 1.12 (t, $J = 7.5$ Hz, 3H), 1.21 (t, $J = 7.5$ Hz, 3H), 1.32–1.45 (m, 2H), 1.57–1.67(m, 2H), 2.35–2.42 (m, 4H), 2.67 (q, $J = 7.5$ Hz, 2H), 6.92 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 12.82$, 13.30, 13.70, 21.81, 22.13, 23.56, 30.21, 36.60, 116.92, 117.39, 117.76, 119.01, 140.45, 151.64 ppm; HRMS calcd for $C_{14}H_{20}N_2$ 216.1627; found 216.1624.

Dienedinitrile 9h: Colorless liquid obtained in 98% yield of the isolated product (333 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.85$ (t, $J = 6.9$ Hz, 3H), 1.22–1.35 (m, 6H), 1.47–1.55 (m, 2H), 2.21–2.27 (m, 2H), 5.66 (t, $J = 1.5$ Hz, 1H), 7.07–7.33 ppm (m, 10H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.98$, 22.41, 26.87, 28.67, 31.34, 35.64, 100.26, 115.24, 116.16, 118.08, 128.64 (2CH), 128.91 (2CH), 129.20 (3CH), 129.76 (2CH), 129.82, 132.69, 133.96, 153.49, 164.77 ppm; HRMS calcd for $C_{24}H_{24}N_2$ 340.1940; found 340.1936.

Dienedinitrile 9i: Colorless liquid obtained in 81% yield of the isolated product (221 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.89$ (t, $J = 6.9$ Hz, 6H), 1.30–1.50 (m, 16H), 2.30–2.36 (m, 4H), 5.43 ppm (t, $J = 1.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 14.01$, 22.48, 26.87, 28.73, 31.43, 35.56, 98.69, 115.61, 163.33 ppm; HRMS calcd for $C_{18}H_{28}N_2$ 272.2253; found 272.2257.

Dienedinitrile 9j: Colorless liquid obtained in 90% yield of the isolated product (194 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.95$ (t, $J = 7.5$ Hz, 6H), 1.31–1.44 (m, 4H), 1.54–1.64 (m, 4H), 2.36 (t, $J = 7.5$ Hz, 4H), 6.97 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.67$, 21.91, 30.05, 34.36, 116.74, 120.59, 138.41 ppm; HRMS calcd for $C_{14}H_{20}N_2$ 216.1627; found 216.1625.

A typical procedure for the preparation of 4-bromodienenitrile 8c from 1,4-dibromo-1,3-butadiene: CuCN (1.1 mmol) was added to 1,4-dibromo-1,3-butadiene (1.0 mmol) in a solution of DMF (5 mL). The reaction mixture was heated to reflux and stirred for 1 h to generate 4-bromodienemononitrile, the formation of which was monitored by GC analysis or TLC. The reaction mixture was filtered, and the solvent was evaporated in vacuo to give a black oil, which was purified by column chromatography (silica gel, Et_2O/hexane 1:30) to afford **8c**.

4-Bromodienenitrile 8c: Colorless liquid obtained in 62% yield of the isolated product (202 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.93$–1.02 (m, 12H), 1.38–1.74 (m, 8H), 1.96–2.61 ppm (m, 8H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.24$, 13.62, 14.34, 14.69, 20.84, 21.44, 21.61 (2CH_2), 31.75, 33.69, 34.71, 39.17, 113.33, 119.32, 126.75, 138.88, 158.04 ppm; HRMS calcd for $C_{17}H_{28}N^{79}Br$ 325.1405; found 325.1407.

A typical procedure for the preparation of pyrridine derivatives 2 and 2*H*-pyrrole derivatives 3 from dienenitrile 7a or 4-halodienenitrile 8 and organolithium reagents: An organolithium reagent, such as *n*BuLi (1.2 mmol, 1.5 M in pentane), was added to dienenitrile **7a** or 4-haoldienenitrile **8** (1.0 mmol) in a solution of a diethyl ether or THF (5 mL) at −78 °C. The reaction mixture was then stirred at room temperature (or at reflux in THF) for 1 h to generate pyridine **2** and/or 2*H*-pyrrole **3**, the formation of which was monitored by GC analysis or TLC. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was purified by column chromatography (silica gel, Et_2O/hexane 1:10) to afford pyridine **2** and/or 2*H*-pyrrole **3**.

Pyridine 2a:[7] Colorless liquid obtained in 32% yield of the isolated product (103 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.78$ (t, $J = 7.5$ Hz, 3H), 0.96–1.10 (m, 9H), 1.30–1.80 (m, 8H), 2.44–2.50 (m, 2H), 2.57–2.63(m, 4H), 2.71–2.77 (m, 2H), 7.29–7.39 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 14.43$, 14.57, 14.92, 15.02, 23.69, 24.53, 24.58 (2CH_2), 31.00, 31.39, 31.47, 37.48, 127.13, 127.95 (2CH), 128.88 (2CH), 131.20, 132.34, 142.44, 148.19, 156.52, 157.14 ppm.

Pyridine 2b: Colorless liquid obtained in 16% yield of the isolated product (48 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.92$–1.07 (m, 15H), 1.36–1.57 (m, 8H), 1.61–1.78 (m, 4H), 2.49–2.54 (m, 6H), 2.66–2.73 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 14.14$, 14.44, 14.88 (2CH_3), 14.99, 23.12, 23.55, 24.50, 24.57 (2CH_2), 30.94 (2CH_2), 31.43, 32.62, 35.17, 37.39, 130.66, 130.72, 147.51, 156.78, 156.98 ppm; HRMS calcd for $C_{21}H_{37}N$ 303.2926; found 303.2922.

Pyridine 2d: Colorless liquid obtained in 6% yield of the isolated product (16 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.98$–1.07 (m, 12H), 1.41–1.56 (m, 6H), 1.63–1.75 (m, 2H), 2.47–2.54 (m, 9H), 2.64–2.69 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 14.51$, 14.80, 14.85, 14.96, 22.53, 23.48, 23.81, 24.43, 24.62, 30.89, 31.30, 31.42, 37.56, 130.96, 131.36, 147.44, 153.46, 156.80 ppm; HRMS calcd for $C_{18}H_{31}N$ 261.2457; found 261.2462.

Pyridine 2e:[8] Colorless liquid obtained in 61% yield of isolated product (163 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.99$ (t, $J = 7.5$ Hz, 3H), 1.13–1.31 (m, 9H), 2.56 (q, $J = 7.5$ Hz, 2H), 2.68–2.75 (m, 4H), 2.83 (q, $J = 7.5$ Hz, 2H), 7.33–7.42 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 14.78$, 15.34, 15.44, 15.57, 21.43, 21.78, 21.98, 28.28, 127.21, 127.98 (2CH), 128.86 (2CH), 132.53, 133.43, 142.18, 149.44, 156.59, 158.24 ppm.

2*H*-Pyrrole 3a: Colorless liquid obtained in 90% yield of the isolated product (273 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.73$–0.97 (m, 15H), 1.35–1.73 (m, 10H), 1.95–2.25 (m, 8H), 2.43–2.48 (m, 2H), 5.04 (dt, $^1J = 15.6$ Hz, $^2J = 1.5$ Hz, 1H), 5.62 ppm (dt, $^1J = 15.6$ Hz, $^2J = 6.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.66$, 13.99, 14.27, 14.46, 14.87, 16.25, 21.88, 22.91, 23.11, 25.80, 27.14, 28.97, 29.65, 30.76, 36.23, 83.44, 129.78, 130.61, 135.89, 164.14, 176.81 ppm; HRMS calcd for $C_{21}H_{37}N$ 303.2926; found 303.2933.

2*H*-Pyrrole 3b: Colorless liquid obtained in 91% yield of the isolated product (276 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.63$–1.00 (m, 12H), 1.30 (s, 9H), 1.38–1.74 (m, 6H), 1.95–2.24 (m, 6H), 2.32–2.37 (m, 2H), 4.99 (dt, $^1J = 15.6$ Hz, $^2J = 1.5$ Hz, 1H), 5.59 ppm (dt, $^1J = 15.6$ Hz, $^2J = 6.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.59$, 14.45, 14.67, 15.00, 15.75, 21.59, 23.74, 25.79, 28.99, 29.04 (3CH_3), 29.11, 35.93, 35.95, 81.59, 130.09, 130.42, 136.17, 165.79, 181.73 ppm; HRMS calcd for $C_{21}H_{37}N$ 303.2926; found 303.2930.

2*H*-Pyrrole 3c: Colorless liquid obtained in 78% yield of the isolated product (204 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.79$–1.02 (m, 12H), 1.33–1.65 (m, 6H), 1.91–2.25 (m, 11H), 5.07 (dt, $^1J = 15.6$ Hz, $^2J = 1.5$ Hz, 1H), 5.64 ppm (dt, $^1J = 15.6$ Hz, $^2J = 6.6$ Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS): $\delta = 13.66$, 14.18, 14.44, 14.85, 16.48, 17.43, 21.92, 22.91, 25.80, 27.19, 28.94, 36.37, 83.52, 129.39, 130.84, 135.91, 164.28, 173.40 ppm; HRMS calcd for $C_{18}H_{31}N$ 261.2457; found 261.2457.

2*H*-Pyrrole 3d: Colorless liquid obtained in 73% yield of the isolated product (236 mg). ^{1}H NMR ($CDCl_3$, TMS): $\delta = 0.76$–1.12 (m, 14H), 1.19–1.31 (m, 2H), 1.45–1.57 (m, 2H), 1.71–1.79 (m, 1H), 1.98–2.40 (m, 7H), 5.18 (dt, $^1J = 15.6$ Hz, $^2J = 1.5$ Hz, 1H), 5.72 (dt, $^1J = 15.6$ Hz, $^2J = 6.6$ Hz, 1H), 7.38–7.40 (m, 3H), 7.60–7.63 ppm (m, 2H); ^{13}C NMR ($CDCl_3$,

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

TMS): δ = 13.62, 14.04, 14.45, 14.90, 16.41, 21.98, 22.61, 25.82, 27.61, 29.15, 36.56, 83.97, 127.68 (2CH), 128.19 (2CH), 128.90, 129.06, 131.16, 135.50, 136.56, 166.08, 174.51 ppm; HRMS calcd for $C_{23}H_{33}N$ 323.2613; found 323.2612.

2*H*-Pyrrole 3e:[8] Colorless liquid obtained in 86% yield of the isolated product (230 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.60 (t, J = 7.2 Hz, 3H), 0.92 (t, J = 7.5 Hz, 3H), 1.12 (t, J = 7.5 Hz, 3H), 1.68 (dd, ^1J = 6.3 Hz, ^2J = 1.5 Hz, 3H), 2.14–2.47 (m, 6H), 5.29 (dq, ^1J = 15.6 Hz, ^2J = 1.5 Hz, 1H), 5.70 (dq, J_1 = 15.6 Hz, ^2J = 6.6 Hz, 1H), 7.38–7.43 (m, 3H), 7.60–7.64 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, TMS): δ = 7.56, 13.24, 14.36, 18.22, 18.58, 19.58, 27.20, 84.13, 124.55, 127.72 (2CH), 128.24 (2CH), 129.01, 130.90, 136.23, 137.13, 166.40, 174.81 ppm.

Imine 17: *n*BuLi (1.2 mmol, 1.5 M in pentane) was added to 4-haoldienenitrile **8a** (1.0 mmol) in a solution of diethyl ether (5 mL) at −50 °C. The reaction mixture was stirred at −50 °C for 1 h and quenched with saturated aqueous $NaHCO_3$ solution, subsequent work-up generated imine **17**. A colorless liquid was obtained in 100% yield of the isolated product (339 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.88–0.98 (m, 15H), 1.32–1.63 (m, 12H), 1.92–2.66 (m, 10H), 8.82 ppm (br, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.54, 13.95, 14.00, 14.60, 14.77, 21.05, 21.70, 21.77, 22.52, 22.71, 28.03, 31.87, 35.07, 36.73, 37.21 ($2CH_2$), 131.98, 137.55, 138.57, 138.71, 184.26 ppm; HRMS calcd for $C_{21}H_{38}N^{35}Cl$ 339.2693; found 339.2690.

A typical procedure for the preparation of iminocyclopentadiene 19a–c from 4-bromodienenitrile 8c and *t*BuLi: *t*BuLi (2.4 mmol, 1.6 M in pentane) was added to 4-bromodienenitrile **8c** (1.0 mmol) in a solution of diethyl ether (5 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h to generate a cyclic *N*-lithioketimine intermediate, the formation of which was monitored by GC analysis or TLC. If the reaction mixture was not quenched, acyl chloride was added and the reaction mixture was further stirred at room temperature for 1 h. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether. The extracts were washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was purified by column chromatography (neutral Al_2O_3, Et_2O/hexane 1:20) to afford iminocyclopentadiene **19a–c**.

Iminocyclopentadiene 19a: Colorless liquid obtained in 100% yield of the isolated product (247 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.88–1.00 (m, 12H), 1.37–1.52 (m, 8H), 2.18–2.25 (m, 8H), 9.61 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ = 14.32, 14.50, 22.92, 24.03, 25.44, 28.28, 126.97, 148.94, 182.43 ppm; HRMS calcd for $C_{17}H_{29}N$ 247.2300; found 247.2297.

Iminocyclopentadiene 19b: Colorless liquid obtained in 88% yield of the isolated product (309 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.80 (t, J = 7.2 Hz, 6H), 0.98 (t, J = 7.2 Hz, 6H), 1.26–1.50 (m, 8H), 2.02–2.23 (m, 8H), 7.42–7.57 (m, 3H), 7.87–7.89 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, TMS): δ = 14.28, 14.53, 22.80, 23.72, 26.30, 28.43, 127.42, 128.49 (2CH), 128.94 (2CH), 132.77, 133.41, 152.12, 170.02, 178.01 ppm; HRMS calcd for $C_{24}H_{33}NO$ 351.2562; found 351.2559.

Iminocyclopentadiene 19c: Colorless liquid obtained in 90% yield of the isolated product (273 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.88 (t, J = 7.2 Hz, 6H), 0.98 (t, J = 7.2 Hz, 6H), 1.19 (t, J = 7.5 Hz, 3H), 1.31–1.51 (m, 8H), 2.01–2.06 (m, 4H), 2.17–2.22 (m, 4H), 2.55 ppm (q, J = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, TMS): δ = 8.87, 14.30, 14.51, 22.79, 23.72, 26.23, 28.39, 31.38, 127.23, 151.52, 166.46, 186.58 ppm; HRMS calcd for $C_{20}H_{33}NO$ 303.2562; found 303.2565.

A typical procedure for the preparation of 2*H*-pyrrole derivatives 20a–i from 1,4-dicyano-1,3-butadiene 9 and organolithium reagents: *n*BuLi (1.2 mmol, 1.5 M in pentane) was added to 1,4-dicyano-1,3-butadiene **9** (1.0 mmol) in a solution of diethyl ether (5 mL) at −50 °C. The reaction mixture was stirred at room temperature for 1 h to generate a 2*H*-pyrrole lithium intermediate, the formation of which was monitored by GC analysis or TLC. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was purified by column chromatography (silica gel, Et_2O/hexane 1:10) to afford **20a** and **20d–i**. For the preparation of **20b,c**: After the addition of *n*BuLi at −50 °C, the reaction mixture was stirred at −50 °C for 1 h. Allyl bromide or benzyl bromide (1.5 mmol) were added at −50 °C and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution. Subsequent work-up afforded 2*H*-pyrrole **20b,c**.

2*H*-Pyrrole 20a: Colorless liquid obtained in 100% yield of the isolated product (330 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.67–1.05 (m, 17H), 1.21–1.84 (m, 14H), 2.03–2.51 (m, 6H), 2.73–3.08 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.53, 13.55, 13.90, 13.92, 14.00, 14.13, 14.40 ($2CH_3$), 15.03, 15.07, 15.71, 16.11, 20.88, 21.13, 21.29, 21.39, 22.90, 22.94, 23.06 ($2CH_2$), 27.09, 27.21, 28.38, 28.71, 29.04, 29.09, 29.74, 29.88, 30.52, 30.58, 36.41, 36.54, 37.93, 38.51, 81.67, 82.08, 120.34, 120.69, 139.58, 139.61, 159.81, 161.09, 178.64, 179.12 ppm; HRMS calcd for $C_{22}H_{38}N_2$ 330.3035; found 330.3030.

2*H*-Pyrrole 20b: Colorless liquid obtained in 100% yield of the isolated product (369 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.55–0.82 (m, 8H), 0.92–1.10 (m, 11H), 1.29–2.06 (m, 12H), 2.13–2.48 (m, 7H), 2.62–2.97 (m, 1H), 4.92–5.19 (m, 2H), 5.67–6.10 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.93 ($2CH_3$), 14.02 ($2CH_3$), 14.26, 14.28, 14.56, 14.61, 15.08, 15.10, 15.66, 15.71, 19.25, 20.20, 21.59, 21.62, 22.97, 23.03 ($2CH_2$), 23.11, 27.20, 27.24, 29.70, 29.79, 29.84, 29.89, 30.60, 30.64, 33.65, 33.72, 34.29, 37.01, 37.38, 40.15, 45.64, 45.66, 85.31, 85.36, 117.99, 118.29, 122.10, 122.22, 133.80, 134.66, 139.94, 140.00, 161.89, 162.06, 178.75, 179.06 ppm; HRMS calcd for $C_{25}H_{42}N_2$ 370.3348; found 370.3335.

2*H*-Pyrrole 20c: Colorless liquid obtained in 90% yield of the isolated product (378 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.32–1.15 (m, 20H), 1.21–1.72 (m, 9H), 2.00–2.61 (m, 9H), 3.28–3.50 (m, 1H), 7.24–7.40 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.95 ($2CH_3$), 14.03, 14.09 ($2CH_3$), 14.59 ($2CH_3$), 15.00, 15.19, 15.63, 15.92, 19.74, 20.77, 21.52, 21.73, 22.94, 23.00, 23.03, 23.18, 27.22, 27.25, 29.72, 29.78, 29.85, 30.15, 30.59 ($2CH_2$), 33.16, 33.58 ($2CH_2$), 36.47, 38.88, 41.99, 46.43, 46.87, 85.52, 85.67, 121.93, 122.22, 127.00, 127.09, 128.18 (2CH), 128.20 (2CH), 130.30 (2CH), 130.60 (2CH), 136.42, 137.05, 140.03, 140.21, 162.02, 162.17, 178.91, 179.50 ppm; HRMS calcd for $C_{29}H_{44}N_2$ 420.3505; found 420.3494.

2*H*-Pyrrole 20d: Colorless liquid obtained in 93% yield of the isolated product (326 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.78–1.65 (m, 22H), 1.78–2.51 (m, 6H), 2.85–3.20 (m, 1H), 7.41–7.61 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.55 ($2CH_3$), 14.00, 14.14 ($2CH_3$), 14.18, 15.03, 15.07, 15.86, 16.27, 20.92, 21.13, 21.39, 21.47, 22.52, 22.54, 27.53, 27.68, 28.45, 28.76, 29.18, 29.23, 36.61, 36.72, 38.00, 38.62, 82.19, 82.56, 120.15, 120.46, 127.43 (2CH), 127.60 (2CH), 128.40 (2CH), 128.45 (2CH), 129.38 (2CH), 135.66, 135.72, 139.41, 139.44, 161.58, 162.83, 176.04, 176.70 ppm; HRMS calcd for $C_{24}H_{34}N_2$ 350.2722; found 350.2715.

2*H*-Pyrrole 20e: Colorless liquid obtained in 95% yield of the isolated product (274 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.66–1.05 (m, 15H), 1.15–2.36 (m, 16H), 2.71–3.04 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.54, 13.57, 13.97, 14.13, 14.32 ($2CH_3$), 15.02, 15.07, 15.73, 16.25, 17.10, 17.17, 20.85, 21.17, 21.28, 21.42, 22.88 ($2CH_2$), 27.15, 27.24, 28.28, 28.76, 29.00, 29.05, 36.48 ($2CH_2$), 37.81, 38.43, 81.77, 82.21, 120.22, 120.63, 139.59, 139.71, 159.75, 161.22, 175.14, 175.60 ppm; HRMS calcd for $C_{19}H_{32}N_2$ 288.2566; found 288.2565.

2*H*-Pyrrole 20f: Colorless liquid obtained in 88% yield of the isolated product (264 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.63–1.11 (m, 11H), 1.20–2.12 (m, 14H), 2.23–2.31 (m, 2H), 2.50–2.94 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.36, 13.43, 13.75 ($4CH_3$), 20.69, 21.25, 21.69, 21.73, 22.65, 22.70, 22.96, 23.00, 24.91, 25.24, 26.07, 26.16, 26.97, 27.48, 27.91, 29.53, 29.64, 29.90, 30.51, 30.60, 34.12, 34.18, 34.90, 38.00, 77.26, 77.80, 118.84, 120.21, 133.59, 134.17, 161.03, 162.99, 178.46, 179.47 ppm; HRMS calcd for $C_{20}H_{32}N_2$ 300.2566; found 300.2568.

2*H*-Pyrrole 20g: Colorless liquid obtained in 75% yield of the isolated product (240 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.75–1.04 (m, 8H), 1.07–2.22 (m, 10H), 2.37–2.44 (m, 2H), 2.64–3.06 (m, 3H), 7.37–7.44 (m, 3H), 7.59–7.66 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.56, 13.62, 13.83, 13.87, 20.92, 21.40, 21.87, 21.94, 22.83, 22.90, 25.42, 25.73, 26.71, 26.93, 27.20, 27.72, 28.19, 30.01, 34.41, 34.62, 35.27, 38.33, 78.05, 78.54, 118.89, 120.20, 127.82 (2CH), 127.86 (2CH), 128.34 (2CH), 128.38 (2CH), 129.25, 129.44, 133.79, 134.18, 135.59, 135.81, 162.96, 164.67, 175.73, 177.20 ppm; HRMS calcd for $C_{22}H_{28}N_2$ 320.2253; found 320.2249.

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2*H*-Pyrrole 20h: Colorless liquid obtained in 85% yield of the isolated product (228 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.38–0.51 (m, 3H), 0.76–1.27 (m, 7H), 1.36–1.58 (m, 3H), 1.75–1.85 (m, 2H), 2.10–2.40 (m, 2H), 2.82–3.26 (m, 3H), 7.40–7.75 ppm (m, 4H); ^{13}C NMR ($CDCl_3$, TMS): δ = 7.34, 7.53, 11.99, 12.51, 13.89, 13.90, 19.71, 20.92, 22.86 (2CH_2), 28.10, 29.51, 29.60, 30.03, 30.35, 30.37, 41.11, 42.34, 79.25, 79.63, 120.11, 120.62, 121.20, 121.42, 122.00, 122.39, 128.27 (2CH), 128.83, 129.15, 140.08, 140.16, 152.06, 152.48, 174.81, 175.20 ppm; HRMS calcd for $C_{18}H_{24}N_2$ 268.1940; found 268.1931.

2*H*-Pyrrole 20i: Colorless liquid obtained in 75% yield of the isolated product (216 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.45–0.58 (m, 3H), 0.83–1.25 (m, 5H), 1.43–3.40 (m, 3H), 7.43–7.97 ppm (m, 9H); ^{13}C NMR ($CDCl_3$, TMS): δ = 7.43, 7.61, 11.98, 12.52, 19.83, 21.03, 28.39, 30.48, 41.27, 42.52, 79.61, 79.94, 120.06, 120.60, 122.31, 122.75, 122.94, 123.14, 128.12, 128.29, 128.36, 128.78, 128.87, 128.93, 129.29, 130.46, 130.58, 133.84, 133.94, 139.05, 139.09, 153.06, 153.53, 171.53, 172.00 ppm; HRMS calcd for $C_{20}H_{20}N_2$ 288.1627; found 288.1628.

A typical procedure for the reaction of different conjugated enenitriles 23, 7a, 8c, 9a, 9d, and 9f with $LiAlH_4$: $LiAlH_4$ (1.0 mmol, 1.0 M in Et_2O) was added to the conjugated enenitrile **23** (or **7a, 8c, 9a, 9d, 9f**; 1.0 mmol) in a solution of diethyl ether (5 mL) at −78 °C. The reaction mixture was stirred at 0 °C (or other proper temperature for different substrates) for 1 h to generate the final product or intermediate, the formation of which was monitored by GC analysis or TLC. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give the crude product, which was purified by column chromatography (silica gel, Et_2O/hexane 1:10 or 100% Et_2O) to afford **24**, **25a**,**b**, **2f**, and **20j–k**.

Nitrile 24: Colorless solid obtained as two isomers (d.r. = 3:1) in a combined yield of 89% of the isolated products (209 mg). Major isomer: ^{1}H NMR ($CDCl_3$, TMS): δ = 0.80 (t, J = 7.5 Hz, 3H), 1.78–1.87 (m, 2H), 2.83–2.94 (m, 1H), 4.04 (d, J = 6.9 Hz, 1H), 7.04–7.09 (m, 4H), 7.22–7.27 ppm (m, 6H); ^{13}C NMR ($CDCl_3$, TMS): δ = 11.99, 26.06, 44.28, 52.54, 119.83, 127.42, 127.97, 128.13 (2CH), 128.35 (2CH), 128.45 (2CH), 128.63 (2CH), 134.51, 139.05 ppm; HRMS calcd for $C_{17}H_{17}N$ 235.1361; found 235.1358.

Amine 25a: Colorless liquid obtained in 85% yield of the isolated product (213 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.84–0.95 (m, 12H), 1.21–1.48 (m, 10H), 1.97–2.13 (m, 8H), 3.21 (s, 2H), 4.99 ppm (t, J = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.94, 14.11, 14.37, 14.60, 21.44, 21.64, 22.27, 23.25, 29.87, 31.26, 31.90, 32.21, 43.60, 127.82, 135.75, 139.91, 140.31 ppm; HRMS calcd for $C_{17}H_{33}N$ 251.2613; found 251.2611.

Amine 25b: Colorless liquid obtained in 80% yield of the isolated product (263 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.88–0.98 (m, 12H), 1.21–1.69 (m, 10H), 1.86–2.00 (m, 2H), 2.15–2.32 (m, 4H), 2.49–2.54 (m, 2H), 3.06–3.28 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.29, 14.45 (2CH_3), 14.90, 21.62, 21.65, 21.79, 21.89, 30.49, 33.61, 35.00, 39.08, 43.91, 124.71, 135.94, 136.35, 140.32 ppm; HRMS calcd for $C_{17}H_{32}N^{79}Br$ 329.1718; found 329.1718.

Pyridine 2f: Colorless liquid obtained in 75% yield of the isolated product (185 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.97–1.07 (m, 12H), 1.42–1.80 (m, 8H), 2.50–2.59 (m, 6H), 2.69–2.74 (m, 2H), 8.14 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, TMS): δ = 14.28, 14.45, 14.82, 14.86, 23.28, 24.18, 24.45, 24.53, 30.73, 30.91, 32.46, 37.32, 133.13, 133.18, 147.33, 147.37, 157.82 ppm; HRMS calcd for $C_{17}H_{29}N$ 247.2300; found 247.2311.

2*H*-Pyrrole 20j: Colorless liquid obtained as two isomers (d.r. = 1:1) in a combined yield of 65% of the isolated products (159 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.60–1.16 (m, 8H), 1.21–2.14 (m, 10H), 2.27–2.35 (m, 2H), 2.58–2.99 (m, 3H), 8.08 (s, 0.6H), 8.12 ppm (s, 0.4H); ^{13}C NMR ($CDCl_3$, TMS): δ = 13.51, 13.62, 13.71 (2CH_2), 20.86, 21.35, 21.72, 21.78, 22.62 (2CH_2), 24.84, 25.19, 26.44, 26.49, 27.04, 27.68, 28.11, 30.02, 34.07, 34.40, 34.62, 38.19, 80.92, 81.38, 118.74, 120.10, 133.77, 134.32, 160.84, 162.83, 167.97, 168.67 ppm; HRMS calcd for $C_{16}H_{24}N_2$ 244.1940; found 244.1946.

2*H*-Pyrrole 20k: Colorless liquid obtained as two isomers (d.r. = 1:1) in a combined yield of 51% of the isolated product (108 mg). ^{1}H NMR ($CDCl_3$, TMS): δ = 0.40–0.56 (m, 3H), 0.78–1.56 (m, 5H), 2.13–2.41 (m, 2H), 2.82–2.87 (m, 0.5H), 3.23–3.28 (m, 0.5H), 7.27–7.75 (m, 4H), 8.55 (s, 0.5H), 8.58 ppm (s, 0.5H); ^{13}C NMR ($CDCl_3$, TMS): δ = 7.25, 7.55, 11.97, 12.42, 19.68, 20.80, 27.93, 29.72, 40.58, 41.83, 81.65, 82.03, 119.91, 120.30, 122.05, 122.22, 122.41, 122.45, 128.51, 128.53, 129.24, 129.51, 139.92, 140.01, 151.69, 151.97, 163.94, 164.22 ppm; HRMS calcd for $C_{14}H_{16}N_2$ 212.1314; found 212.1313.

Acknowledgements

This work was supported by the National Natural Science Foundation of China. C.Y.W. thanks the Postdoctorate Research Fund of China (2005038003) for financial support. The Cheung Kong Scholars Program, Dow Corning Corporation, Qiu Shi Science & Technologies Foundation, and BASF are gratefully acknowledged.

[1] For recent reviews on the reaction of organolithium reagents with organonitriles to afford pyridine derivatives and related compounds, see: a) F. Foubelo, M. Yus, *Current. Org. Chem.* **2005**, *9*, 459–490; b) P. Langer, W. Freiberg, *Chem. Rev.* **2004**, *104*, 4125–4149; c) C. Najera, J. M. Sansano, M. Yus, *Tetrahedron* **2003**, *59*, 9255–9303.

[2] Reactions of mono-organolithium compounds with nitriles: a) R. M. Anker, A. H. Cook, *J. Chem. Soc.* **1941**, 323–331; b) A. A. Scala, N. M. Bikales, E. I. Becker, *J. Org. Chem.* **1965**, *30*, 303–304; c) D. J. Berry, B. J. Wakefield, *J. Chem. Soc. C* **1971**, 642–645; d) D. J. Berry, J. D. Cook, B. J. Wakefield, *J. Chem. Soc. Perkin Trans. 1* **1972**, 2190–2192; e) L. S. Cook, B. J. Wakefield, *Tetrahedron Lett.* **1976**, *2*, 147–150; f) L. S. Cook, B. J. Wakefield, *J. Chem. Soc. Perkin Trans. 1* **1980**, 2392–2397; g) D. Seyferth, R. C. Hui, W. Wang, *J. Org. Chem.* **1993**, *58*, 5843–5845; h) D. R. Armstrong, W. Clegg, M. MacGregor, R. E. Mulvey, P. A. O'Neil, *J. Chem. Soc. Chem. Commun.* **1993**, 608–610; i) D. R. Armstrong, K. W. Henderson, M. MacGregor, R. E. Mulvey, M. J. Ross, W. Clegg, P. A. O'Neil, *J. Organomet. Chem.* **1995**, *486*, 79–93; j) S. C. Ball, R. P. Davies, P. R. Raithby, G. P. Shields, R. Snaith, *J. Organomet. Chem.* **1998**, *550*, 457–461; k) C. M. Coleman, D. F. O'Shea, *J. Am. Chem. Soc.* **2003**, *125*, 5054–5055.

[3] Recent work on the reaction of organolithium reagents with organonitriles that leads to the formation of pyridine compounds, see: a) H. M. Hansen, M. Lysen, M. Begtrup, J. K. Kristensen, *Tetrahedron* **2005**, *61*, 9955–9960; b) J. K. Kristensen, P. Vedso, M. Begtrup, *J. Org. Chem.* **2003**, *68*, 4091–4092; c) J. Pawlas, M. Begtrup, *Org. Lett.* **2002**, *4*, 2687–2690; d) M. Lysen, J. L. Kristensen, P. Vedso, M. Begtrup, *Org. Lett.* **2002**, *4*, 257–259; e) J. Pawlas, P. Vedso, P. Jakobsen, P. O. Huusfeldt, M. Begtrup, *J. Org. Chem.* **2001**, *66*, 4214–4219.

[4] D. J. Jakiela, P. Helquist, L. D. Jones, *Org. Synth.* **1984**, *62*, 74–85.

[5] For recent reviews on the synthesis of pyridine derivatives, see: a) J. A. Varela, C. Saa, *Chem. Rev.* **2003**, *103*, 3787–3901; b) G. Jones, *Comprehensive Heterocyclic Chemistry; Vol. 5* (Eds.: A. R. Katritzky, C. W. Rees, V. F. V. Scriven), Pergamon, Oxford, **1996**, p. 167; c) D. B. Grotjahn, *Comprehensive Organometallic Chemistry II, Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, p. 741; d) G. D. Henry, *Tetrahedron* **2004**, *60*, 6043–6061; e) G. R. Newkome, A. K. Patri, F. Holder, U. S. Schubert, *Eur. J. Org. Chem.* **2004**, 235–254; f) Z. Xi, Z. Li, *Topic Organomet. Chem.* **2004**, *8*, 27–56.

[6] For recent reviews on the synthesis of pyrrole derivatives, see: a) T. Y. Luh, C. F. Lee, *Eur. J. Org. Chem.* **2005**, 3875–3885; b) R. J. Sundberg, *Comprehensive Heterocyclic Chemistry; Vol 2* (Eds.: A. R. Katritzky, C. W. Rees, V. F. V. Scriven), Pergamon, Oxford, **1996**, p. 119; c) G. W. Gribble, *Comprehensive Heterocyclic Chemistry; Vol. 2* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Pergamon, Oxford, **1996**, p. 207; d) R. A. Jones, *Pyrroles, Part II, The Synthesis, Reactivity and Physical Properties of Substituted Pyrroles*; Wiley, New York, **1992**, p. 628; see also: e) P. Mathew, C. V. Asokan,

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Tetrahedron **2006**, *62*, 1708–1716; f) L. Lu, G. Chen, S. Ma, *Org. Lett.* **2006**, *8*, 835–838, and references therein.

[7] J. Chen, Q. Song, C. Y. Wang, Z. Xi, *J. Am. Chem. Soc.* **2002**, *124*, 6238–6239.

[8] C. Y. Wang, Z. Wang, L. Liu, C. Wang, G. Liu, Z. Xi, *J. Org. Chem.* **2006**, *71*, 8565–8571.

[9] a) F. F. Fleming, B. C. Shook, T. Jiang, O. W. Steward, *Org. Lett.* **1999**, *1*, 1547–1550; b) P. A. Zoretic, H. Fang, A. A. Ribeiro, *J. Org. Chem.* **1998**, *63*, 7213–7217; c) Y. A. Sharanin, M. P. Goncharenko, V. P. Litvinov, *Uspekhi Khimii* **1998**, *67*, 442–473.

[10] a) F. F. Fleming, Q. Z. Wang, *Chem. Rev.* **2003**, *103*, 2035–2077; b) F. F. Fleming, Y. Pu, F. Tercek, *J. Org. Chem.* **1997**, *62*, 4883–4885; c) F. F. Fleming, Z. Hussain, D. Weaver, R. E. Norman, *J. Org. Chem.* **1997**, *62*, 1305–1309.

[11] a) J. H. Hall, *J. Am. Chem. Soc.* **1965**, *87*, 1147–1148; b) D. J. Pasto, N. Z. Huang, S. H. Yang, C. W. Eigenbrot, R. D. Barreto, T. P. Fehlner, *J. Org. Chem.* **1985**, *50*, 5056–5060; c) I. Kovacik, C. Scriban, D. S. Glueck, *Organometallics* **2006**, *25*, 536–539; d) H. W. Whitlock, Jr., C. R. Reich, R. L. Machezich, *J. Am. Chem. Soc.* **1970**, *92*, 6665–6667.

[12] a) W. S. Wadsworth, Jr., *Org. React.* **1977**, *25*, 73–253; b) H. Takayanagi, Y. Kitano, Y. Morinaka, *J. Org. Chem.* **1994**, *59*, 2700–2706.

[13] a) Y. L. Benanni, *J. Org. Chem.* **1996**, *61*, 3542–3544; b) H. Westmijze, H. Kleijn, P. Vermeer, *Synthesis Synthesis.* **1978**, 454–456; c) H. Kleijn, H. Westmijze, J. Meijer, P. Vermeer, *J. Organomet. Chem.* **1981**, *206*, 257–264.

[14] a) M. Prochazka, M. Siroky, *Collect. Czech. Chem. Commun.* **1983**, *48*, 1765–1773; b) J. Lindley, *Tetrahedron* **1984**, *40*, 1433–1456; c) L. A. Hammad, P. G. Wenthold, *J. Am. Chem. Soc.* **2003**, *125*, 10796–10797.

[15] For recent applications of the nucleophilic substitution of aryl halides using CuCN, see: a) C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer, G. G. Malliaras, *Org. Lett.* **2005**, *7*, 3163–3166; b) H. Kawai, R. Katoono, K. Fujiwara, T. Tsuji, T. Suzuki, *Chem. Eur. J.* **2005**, *11*, 815–824; c) C. B. Nielsen, T. Bjornholm, *Org. Lett.* **2004**, *6*, 3381–3384; d) J. N. Moorthy, P. Mal, N. Singhal, P. Venkatakrishnan, R. Malik, P. Venugopalan, *J. Org. Chem.* **2004**, *69*, 8459–8466.

[16] For preparative methods of 1-halo-1,3-diene derivatives, see: a) T. Takahashi, D. Y. Kondakov, Z. Xi, N. Suzuki, *J. Am. Chem. Soc.* **1995**, *117*, 5871–5872; b) T. Takahashi, W. Sun, C. Xi, H. Ubayama, Z. Xi, *Tetrahedron* **1998**, *54*, 715–726; c) H. Ubayama, W. Sun, Z. Xi, T. Takahashi, *Chem. Commun.* **1998**, 1931–1932.

[17] For preparative methods of 1,4-dihalo-1,3-diene derivatives, see: a) E. Negishi, F. E. Cederbaum, T. Takahashi, *Tetrahedron Lett.* **1986**, *27*, 2829–2832; b) E. Negishi, S. J. Holmes, J. M. Tour, J. A. Miller, F. K. Cederbaum, D. R. Swanson, T. Takahashi, *J. Am. Chem. Soc.* **1989**, *111*, 3336–3346; c) S. L. Buchwald, R. B. Nielsen, *J. Am. Chem. Soc.* **1989**, *111*, 2870–2874; d) J. E. Hill, G. Balaich, P. E. Fanwick, I. P. Rothwell, *Organometallics* **1993**, *12*, 2911–2924; e) S. Yamaguchi, R. Jin, K. Tamao, F. Sato, *J. Org. Chem.* **1998**, *63*, 10060–10062; f) Z. Xi, Z. Song, G. Liu, X. Liu, T. Takahashi, *J. Org. Chem.* **2006**, *71*, 3154–3158.

[18] B. J. Wakefield, *The Chemistry of Organolithium Compounds*; Pergamon, Oxford, **1974**, pp. 116–121.

[19] a) J. Ichikawa, Y. Wada, H. Miyazaki, T. Mori, H. Kuroki, *Org. Lett.* **2003**, *5*, 1455–1458; b) K. Kobayashi, K. Yoneda, K. Miyamoto, O. Morikawa, H. Konishi, *Tetrahedron* **2004**, *60*, 11639–11645; c) K. Kobayashi, K. Yoneda, M. Mano, O. Morikawa, H. Konishi, *Chem. Lett.* **2003**, *32*, 76–77; d) K. Kobayashi, T. Shiokawa, O. Morikawa, H. Konishi, *Chem. Lett.* **2004**, *33*, 236–237; e) T. Mori, J. Ichikawa, *Chem. Lett.* **2004**, *33*, 590–591.

[20] R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299–338.

[21] L. H. Amundsen, L. S. Nelson, *J. Am. Chem. Soc.* **1951**, *73*, 242–244.

[22] a) A. Buschauer, A. Friese-Kimmel, G. Baumann, W. Schunack, *Eur. J. Med. Chem.* **1992**, *27*, 321–330; b) S. Akabori, K. Takahashi, M. Ohtomi, Y. Sakamoto, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3867–3868; c) Y. Yamamoto, S. Nishii, T. Ibuka, *J. Chem. Soc. Perkin Trans. 1* **1989**, 1703–1705; d) P. T. Lansbury, C. A. Mojica, *Tetrahedron Lett.* **1986**, *27*, 3967–3970.

[23] For cleavage of the C≡N bond in the reduction of nitriles with $LiAlH_4$, see: J. M. Mattalia, A. Samat, M. Chanon, *J. Chem. Soc. Perkin Trans. 1* **1991**, *7*, 1769–1770.

[24] Copies of ^1H and ^{13}C NMR spectra for new compounds are given in the Supporting Information.

Received: January 9, 2007
Published online: May 11, 2007

 © 2007 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim