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Radical Annulation Reactions of Allyl Iodomalononitriles

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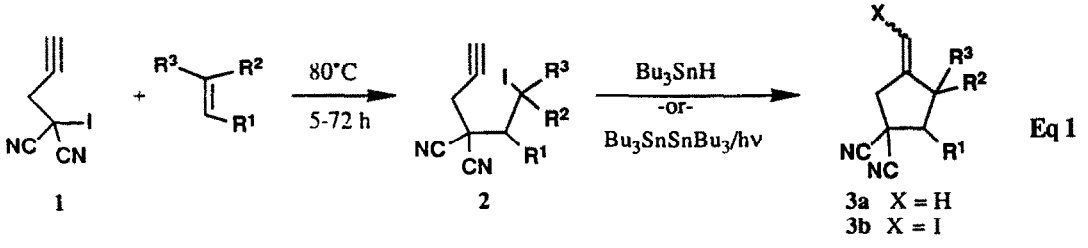
Summary: Heating of allyl iodomalononitriles with alkenes, followed by tin hydride reduction, forms 1-(cyanalkyl)-4-cyanocyclopentane rings with up to 5 new stereocenters by a sequence of atom transfer addition followed by nitrile transfer cyclization.

Introduction: Radical annulation reactions are rapidly emerging as a powerful means to append functionalized five-membered rings to alkenes.[2] Annulation reactions of electrophilic radicals are especially useful because simple alkenes (lacking any activating groups) can be used as partners.[2] In first generation experiments, we conducted successful annulations with mono- or 1,1-disubstituted alkenes and allyl or propargyl iodomalonic esters.[3a] We have recently introduced a second generation of reagents,[3b,4] iodomalononitriles, which significantly extend the scope of annulation reactions of electrophilic radicals by reacting with mono-, di-, and trisubstituted alkenes. Eq 1 summarizes a typical annulation with propargyl iodomalononitrile **1**.[4] Heating of **1** with an alkene usually produces an intermediate adduct **2**. This adduct (which can often be isolated) is either reduced with tributyltin hydride to give **3a**, or isomerized under standard conditions for atom transfer cyclization to give **3b**.

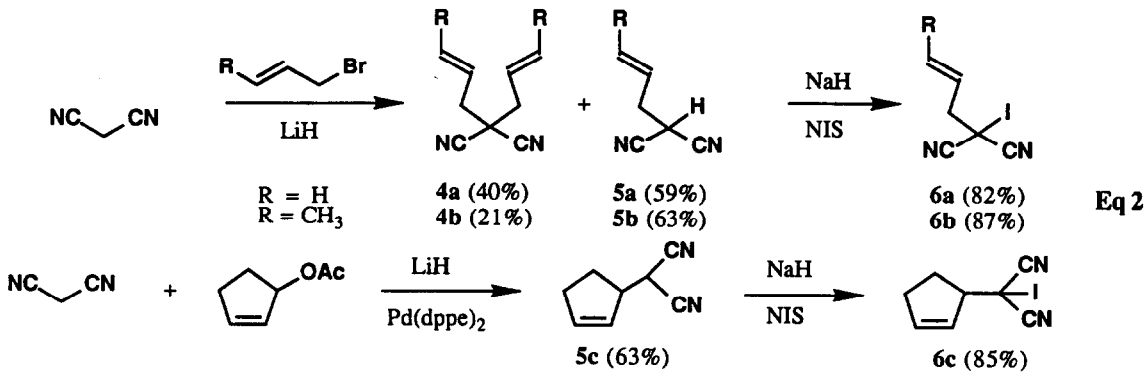


1 **2** **3a** X = H, **3b** X = I

Eq 1

This paper reports full details of a study on radical annulation reactions with allyl iodomalononitriles.[3b] The addition step is very similar to that of the propargyl analog **1**,[4] but the cyclization step provides an interesting twist because it is usually followed by a nitrile transfer reaction. The overall annulation produces two new C–C bonds, one ring, and up to five new stereocenters (often with good to excellent levels of stereocontrol).

Results and Discussion. Equation 2 summarizes the preparation of the three allyl iodomalononitriles that we used in this study. We prepared monoalkylated malononitriles **5a** and **5b** by a standard malononitrile alkylation with lithium hydride and allyl or crotyl bromide. Diallylation was a problem in each case, but yields were high and chromatographic separation to obtain pure **5a,b** was possible. Substrate **5c** was prepared by a Trost-Tsuji reaction.[5] Although some diallylated product still formed (<10%), this palladium catalyzed procedure appears to offer significant advantages over standard procedures for minimizing diallylation. The monoalkylated malononitriles were iodinated by applying the procedure developed for propargyl iodomalononitrile.[4,6] All three iodides **6a-c** were stable to flash chromatography, and could be stored for up to three months at –20°C. Like **1** and iodomalonic esters,[6] iodides **6a-c** are light sensitive.

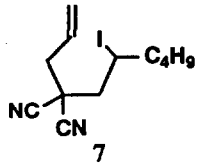
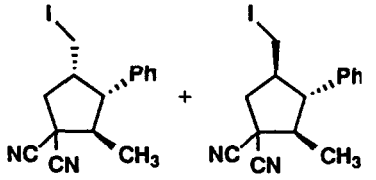
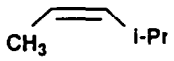
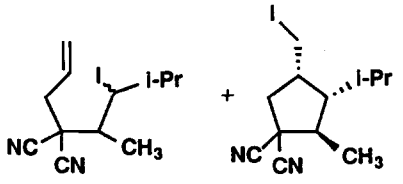
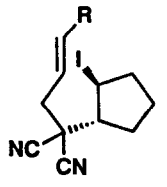
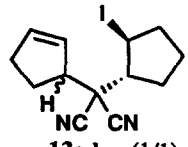
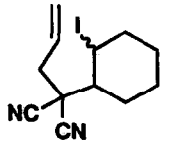


We reacted allyl iodomalononitriles **6a-c** with several alkenes under the standard conditions developed for reactions of **1**.[4] These involve simply heating of **6a** and the alkene (2 equiv) in the dark at 80°C in benzene (0.3M) until the starting iodide is consumed. Table 1 summarizes the results of this series of experiments. The observations with **6a-c** were similar to those with **1**, and the preceding full paper provides a detailed discussion.[4] There is excellent evidence that radical intermediates are involved.[7] Products from these thermolyses were isolated by flash chromatography. Reactions times with **6a-c** were longer than those with **1**, and isolated yields with **6a-c** were marginally (entries 1-4) to significantly (entry 7) lower than those obtained with **1**. Isolation of these products is probably not necessary, since we have shown that direct reductions of crude adduct mixtures from iodide **1** produces products **3a** in comparable (sometimes better) yields than when isolated adducts **2** are used.

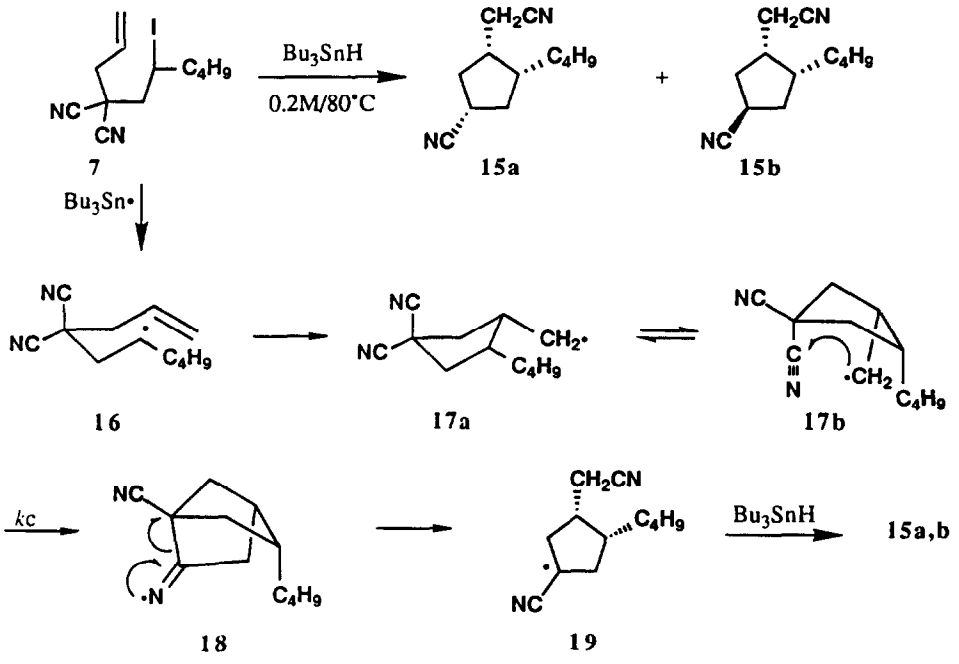
In most cases, the thermal reaction stopped at the adduct stage because the rate of iodine abstraction exceeded that of cyclization.[4] Stereoselectivity for the iodine abstraction is low for acyclic (except benzylic[7]) and cyclic six-membered substrates, but cyclic five-membered substrates exhibit high trans selectivity (entries 4-6). This selectivity (or lack thereof) is of no consequence for the subsequent step. With *cis*-4-methyl-2-pentene (entry 3), cyclization competed with iodine transfer, and a separable mixture of cyclic **11b** and acyclic **10a,b** products formed. The cyclic iodide **11** was mainly one stereoisomer (see below). Reaction of **6a** with β-methyl styrene (entry 2) produced an intermediate adduct (not shown) that was not stable to the reactions conditions, but instead suffered atom transfer cyclization. We continued to heat this reaction until all of the intermediate acyclic adduct had isomerized to the cyclic products. We separated stereoisomers **8** and **9**, and our preliminary assignment of relative stereochemistry was later confirmed by an x-ray crystal structure of **8**.[8]

The second stage of this radical annulation is accomplished by reduction of the initial adduct with tributyltin hydride. Based on literature precedent,[9] we hoped to see nitrile transfer follow radical cyclization, but we were unprepared for the speed with which this nitrile transfer occurred. Equation 3 illustrates a typical result. Reduction of **7** with Bu_3SnH at 0.1M (80°C, benzene) produced a mixture of two major products in a ratio of 2.9/1 along with several very minor products (<5%). The two major products could be separated from the minor products but not from each other, and we obtained a mixture of **15a,b** in 82% yield after flash chromatography. That both **15a** and **15b** resulted from nitrile transfer was evident from inspection of the ^{13}C and ^{1}H NMR spectra of the mixture (see Experimental). However, assigning the configurations of **15a,b** was not so easy with only two of the four possible isomers in hand. Our tentative assignment is based on the mechanistic analysis outlined in eq 3. Abstraction of iodine from **7** gives radical **16**, which suffers very rapid 5-exo cyclization due to the geminal cyano groups.[10] Following Beckwith's guidelines[11] and the Spellmeyer-Houk analysis,[12] we further propose that the major cyclic radical **17a** should be derived from chair-like transition state (TS) **16** with the butyl substituent in a pseudo-equatorial

Table 1. Thermal Reactions of 6a-c With Alkenes

Entry	Iodide	Alkene	Time	Yield	Products
1	**6a**		20 h	92%	 **7**
2	**6a**		80 h	97%	 **8** (2.4/1) **9**
3	**6a**		72 h	65%	 **10a,b** (3.3/1/4.4) **11**
4	**6a**		24 h	71%	 **12a** R = H
5	**6b**[b]		24 h	82%	**12b** R = CH_3
6	**6c**		20 h	48%	 **13a,b** (1/1)
7	**6a**		24 h	37%	 **14** cis/trans (1.5/1)

orientation. In the absence of the geminal cyano group, another chair-like TS (C_4H_9 pseudo-axial) and a boat-like TS[12] could conspire to give trans isomers, but both of these transition states should be disfavored by 1,3 diaxial-like interactions with either the alkene or the butyl group and the axial cyano group. Radical **17a** is highly flexible, and cyclization to a cyano group can occur in conformations like **17b**. The intermediate bicyclo[2.2.1] iminyl radical **18** now fragments rapidly to give α-cyano radical **19**. The two stereoisomers **15a,b** now arise by hydrogen abstraction by **19** from Bu_3SnH, and the major isomer should result from hydrogen abstraction on the less hindered face of **19**. Even though assumptions are required at several points, we are reasonably confident that this stereochemical analysis is correct.[13]

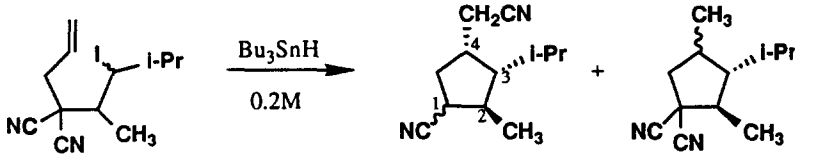


Eq 3

Given the number of possible products, the selectivity in this reaction is remarkable. At least eight products could have formed: one product of direct reduction (without cyclization), two stereoisomers from 5-exo cyclization without nitrile transfer, four stereoisomers from 5-exo cyclization with nitrile transfer, and one product from 6-endo cyclization without nitrile transfer (nitrile transfer in the 6-endo product is not likely because 4-exo cyclization is required). Radical cyclizations to nitriles are known,[14] although the nitrile is not a highly reactive radical acceptor.[15] Thus, the observation that **17** efficiently closes to **18** at relatively high tin hydride concentration surprised us.[16] We observed no products of nitrile transfer during the atom transfer reaction, so this cyclization (**17b** → **18**) is not faster than iodine transfer. In principle, iminyl radical **18** might abstract a hydrogen from tin hydride faster than it fragments; however, the strain in **18** conspires with the stability of product radical **19** to dictate very rapid fragmentation. We observed several minor products in this reaction, but they were present in such small amounts that we did not attempt to identify their structures.

Equation 4 summarizes the results from reduction of the epimeric iodides **10a,b** under the same conditions. Again, two major nitrile transfer products **20a,b** formed, this time in a ratio of 5/1 (52% isolated yield of the mixture). This mixture also contained trace amounts (~2% each) of two compounds that we assigned as products **21** resulting from failure of nitrile transfer. The selectivity in this reaction is even more remarkable than before: according to the above analysis, there are now 15 possible isomeric products![17]

We were only able to obtain complete spectral data for the major isomer, so the tentative stereochemical assignment again rests solely on a mechanistic analysis. This analysis is considerably less certain than that in eq 3. We are aided by the observation that a single cyclic product **11** already forms in the atom transfer reaction.[18] This implies that the two isomers form in the hydrogen transfer step. Further, we know from related cyclizations of alkynes that the methyl and isopropyl groups are oriented trans.[4] Following Beckwith's chair TS model,[10,11] the isopropyl and cyanomethyl substituents should be cis. The major product **20a** is then assigned by assuming that hydrogen will be delivered trans to the C2 methyl group. There are at least two places where this analysis might be wrong: 1) the large isopropyl group might prefer to provide a trans product in the radical cyclization (**20a** is 4,3-trans), or 2) the combined steric effect of the cyanomethyl and isopropyl groups might be large enough to direct hydrogen transfer cis to the methyl group (reverses assignment of **20a, b**). The second possibility is not easily dismissed (see below).



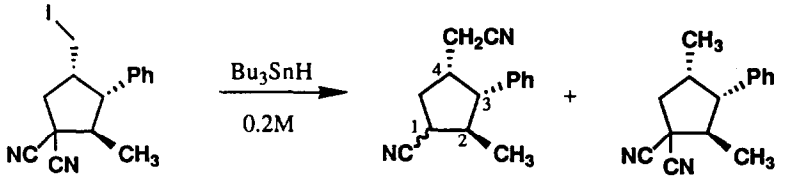
Eq 4

10a,b

20a 1β-CN 20/1 **21a,b**
20b 1α-CN

The products derived from β-methylstyrene provided an interesting opportunity to investigate the nitrile transfer reaction alone because the cyclization already occurred during the first step (Table 1, entry 3). Further, the two stereoisomers that formed could be separated and their relative stereochemistry could be securely assigned. Thus, the only open questions in the reduction of **8** and **9** are: How fast does nitrile transfer occur, and what is the stereochemistry of hydrogen transfer?

Reduction of **8** (eq 5) with tributyltin hydride (0.2M) provided all three possible products **22a, 22b,** and **23** in a ratio of 1.7/1.9/1 (87%). The two major products resulted from nitrile transfer, and configuration at C1 could be assigned with a good level of confidence by comparing the γ gauche effects in the ^{13}C NMR spectra.[19] The stereochemistry of **23** must be the same as the precursor **8**.



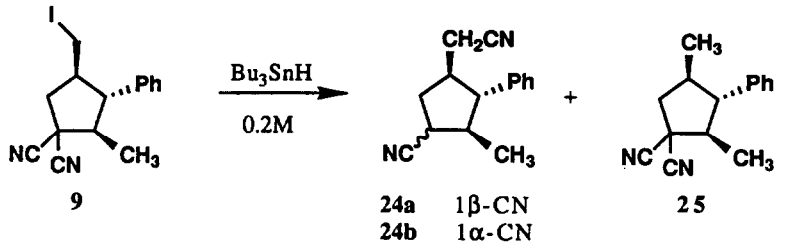
Eq 5

8

22a 1β-CN
22b 1α-CN

23

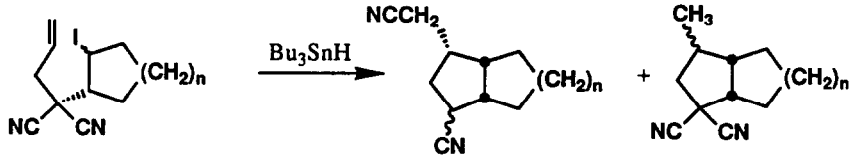
Reduction of **9** (eq 6) gave three different isomers, **24a, 24b,** and **25** in a ratio of 0.6/1/0.9 (78%). We again assigned the configurations of the two nitrile transfer products by ^{13}C NMR. Comparing the results, the nitrile transfer reaction of **9** is slightly slower than that of **8**, while both are significantly slower than **6** and **7**. However, we have used very high tin hydride concentrations for these reductions, and dilution would certainly increase the yield of the nitrile transfer products (**22** or **24**) at the expense of the directly reduced products (**23** or **25**). In each case, the major stereoisomer of the nitrile transfer product originates from hydrogen transfer to the face opposite the C2 methyl group; however, the selectivities are very low. These selectivities cast doubt on the assumption that this methyl group directs hydrogen transfer in eq 4.



Eq 6

If we were to conduct a one step annulation by heating β-methylstyrene and **6a**, and then reducing with a low tin hydride concentration (to suppress reduction prior to nitrile transfer), we would produce **22a/22b/24a/24b** in an approximate ratio of 2.6/2.4/1.3/1. Thus, the selectivity in both the radical cyclization and the hydrogen transfer is considerably lower relative to the previous two substrates. The reasons for this are not obvious to us. Stereoselectivity might be eroded if the initial radical cyclization to the alkene were reversible, and it is known that benzylic radical cyclizations do not always give kinetic products.[20] However, our results suggest that initial cyclic radicals are not interconvertable; if they were, then products in eqs 5 and 6 would have crossed over because reverse cyclizations of the radicals derived from **8** and **9** produce the same radical. Since radical trapping is more efficient under the iodine transfer conditions than the tin hydride conditions, initial products **8** and **9** are probably kinetically controlled.[21]

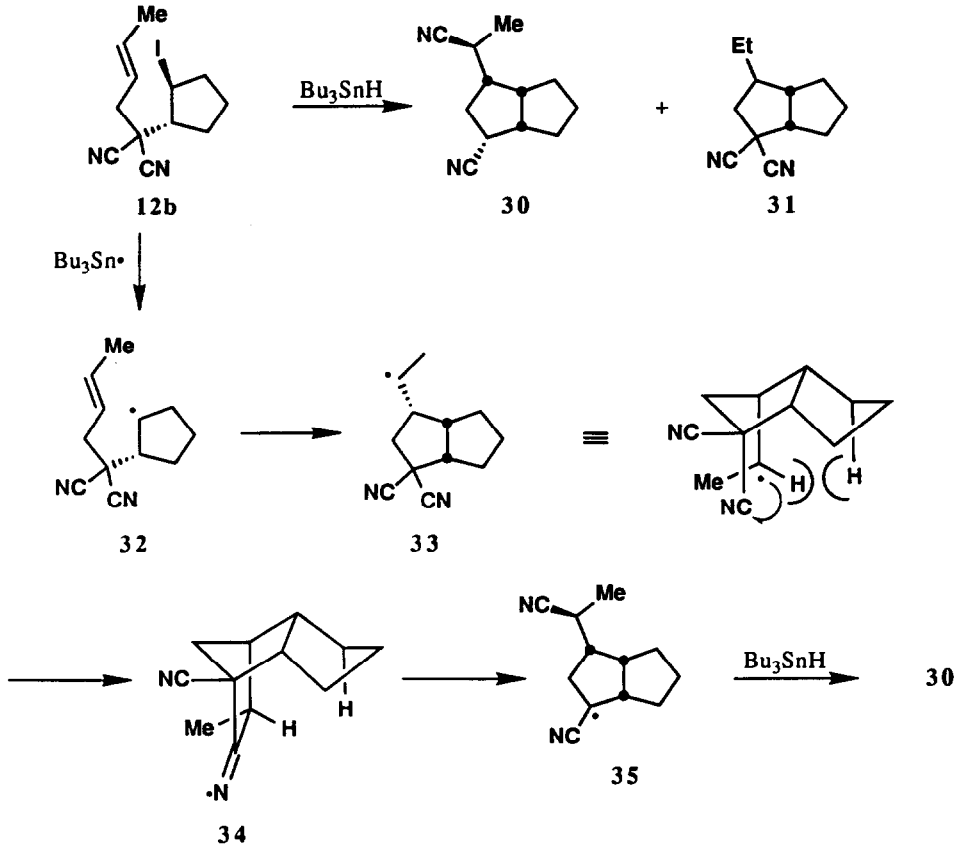
Nitrile transfer reactions also accompany reductive radical cyclizations of the adducts derived from cyclic alkenes (eq 7). When we reduced cyclopentyl iodide **12a** under the standard conditions (Bu_3SnH, 0.2M), we isolated nitrile transfer product **26a** and reduced product **27** in yields of 70 and 16%. The relative stereochemistry of **26** is securely assigned from mechanistic considerations (see the more detailed analysis in eq 8). Two experiments at different tin hydride concentrations quickly showed that reduced product **27** has the same configuration as **26a** at the methyl-bearing carbon. When **12a** was reduced at 1.0M tin hydride concentration, the ratio of **26a/27** decreased from 4.4/1 to 1.2/1. In contrast, when the tin hydride concentration was diluted to 0.03M, only **26a** was detected. In addition to showing that **26a** and **27** have the same relative configuration, these results support our contention that ratios of all the nitrile transfer products (relative to the directly reduced products) can be increased by reducing the tin hydride concentration. Reduction of the cyclohexyl iodide **14** was not quite as clean, producing an inseparable mixture of 4 products in a ratio of 14/2/2/1. We assign major nitrile transfer product structure **28a**, while the two intermediate products are reduced products **29a** and **29b**. The minor product is probably **28b**. The selectivity in this reaction is still quite useful, especially if one considers that a reduction at lower tin hydride concentration would surely increase the ratio of **28a** at the expense of **29a**.



Eq 7

Iodide **12b** provided the most exciting results of all (eq 8). We conducted its reduction at a tin hydride concentration of 0.1M, and we isolated two products in yields of 75% and 4%. The minor product is direct reduction product **31**, but we are uncertain of the configuration at the ethyl-bearing carbon. The relative stereochemistry of the major product **30** follows from the analysis in eq 8. Iodine abstraction from **12b**

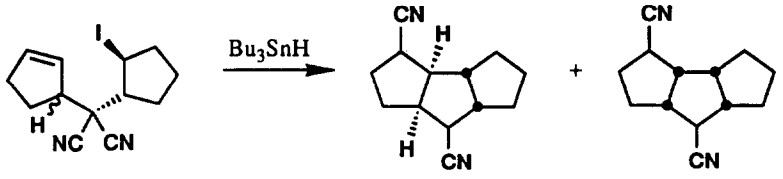
generates radical **32**, which we expect to undergo 5-exo cyclization to orient the new radical-bearing substituent endo to the forming bicyclooctane.[22] If anything, the geminal dicyano group increases this endo selectivity in the cyclization of **32** to **33** compared to existing precedents.[22] Transannular cyclization of **33** should now produce **34**. The alternative transition state, in which the methyl and hydrogen on the radical center are interchanged, must be considerably higher in energy because of severe 1,3 interactions. Fragmentation of **34** gives **35**, which in turn will surely abstract a hydrogen from the exo face of the bicyclooctane **22** to produce **30**.[23]



Overall, starting from two simple, achiral precursors (**1a** and cyclopentene), we have formed one ring, three C–C bonds (while breaking one), and five stereogenic centers with an excellent level of selectivity (≥ 20/1) in 68% yield! Such a rapid increase in complexity is rivaled by only few other cyclopentane annulations. This example also shows that nitrile transfer reactions (and by implication, other radical cyclization/fragmentation reactions) are excellent candidates for controlling acyclic stereochemistry by temporary formation of a ring. Direct control of acyclic stereochemistry in radical reactions has only recently become possible,[24] and we believe that the synthesis of **30** is the first example of the alternative strategy of controlling acyclic stereochemistry in a cyclization/fragmentation process.[25]

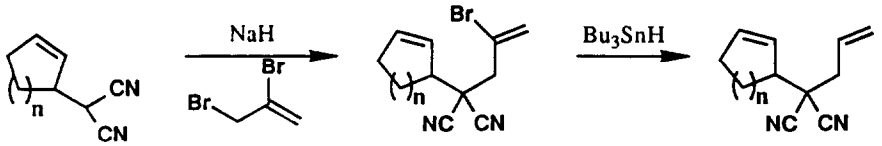
We investigated the nitrile transfer reactions of **13** only briefly (eq 9). This system has the additional complication that **13** is already a 1/1 mixture of stereoisomers. Reduction of **13** with tributyltin hydride (0.1M) produced four isomeric products (by GC-MS) in a ratio of 6.3/5.0/3.3/1. Flash chromatography did not separate the isomers, and the mixture was obtained in 87% yield. As best we can tell from the ^{13}C

NMR,[26] all four products result from nitrile transfer, and are stereoisomers of **36** (derived from one isomer of **13**) and **37** (derived from the other). Even though the stereoselectivity is not high, the facility of the nitrile transfer is remarkable given the strained intermediate iminyl radical that must be involved (see **43** in eq 10).



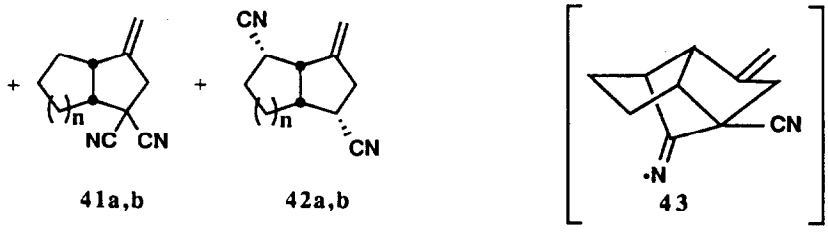
13a,b **36** **37** **Eq 9**

Eq 10 shows the nitrile transfer reactions of two related substrates, **5c** and **38**, which we prepared by standard alkylation reactions. Reduction of **5c** with tin hydride at 0.3M provided three separable products in a ratio of 1/1/0.8 (85%). These were: directly reduced product **40a**, cyclized product **41a**,[27] and nitrile transfer product **42a**. Structure **43** represents the presumed iminyl radical intermediate on the way to **42a**. A nitrile group can only transfer on the endo face of the bicyclooctane. A subsequent experiment showed that reducing the concentration of tin hydride increased the amount of **42a** at the expense of both **41a** and **40a**.[28] This provides evidence that cyclization and nitrile transfer are in direct competition with hydrogen abstraction, as expected. Since vinyl radicals are often highly efficient in cyclizations,[29] the formation of **40a** is surprising. Reduction of the homolog **38** at 0.3M produced **40b**, **41b**, and **42b** (3.0/1/3.0) in 83% yield.



5c n = 1
38 n = 2

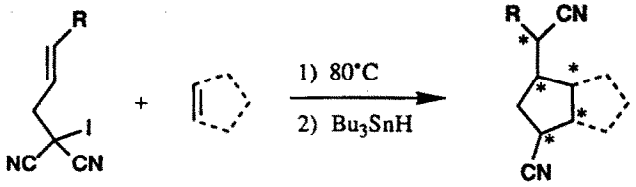
39a,b **40a,b** **Eq 10**



41a,b **42a,b** **43**

Conclusions: The combination of an atom transfer reaction of an alkene with an allyl iodomalononitrile, followed by reductive cyclization with concomitant nitrile transfer, has the potential to become a powerful synthetic protocol (eq 11). Starting from an unactivated alkene, a functionalized ring is added with good overall efficiency, and there are opportunities to control both cyclic and acyclic stereochemistry. To gain a better understanding of the processes involved, we have conducted these reactions in two steps (hence they are not true "annulations"); however, we see no reason why comparable results will not be obtained in a one pot method where the alkene and the iodomalononitrile are first heated to form an adduct, which is then directly reduced with tin hydride (at an appropriate concentration) prior to isolation. We have deliberately conducted our nitrile transfer reactions at very high tin hydride concentrations to gage the efficiency of nitrile transfer. Clearly, higher yields of nitrile transfer products will be obtained by reducing

the tin hydride concentration, as we showed in two examples. Allyl iodomalononitriles combine with propargyl iodomalononitriles to form a unique class of reagents for annulation of funtionalized cyclopentane rings to alkenes.



Eq 11

Experimental

General: See previous paper.[4]

General Procedure for the Alkylation of Malononitrile.

To the solution of iodide or bromide (1.0 mmol) in THF (35-100 mL) was cautiously added the anion of malononitrile [prepared with malononitrile (0.5-1.0 mmol) and LiH (0.55-1.1 mmol) in THF (30 mL)] via a cannula. The mixture was allowed to stir for 3-6 h at 50 °C, poured into cold water, and extracted with ether. The ether solution was washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification of the residue was accomplished by flash column chromatography (silica gel, EtOAc in hexanes) to give the mono- and dialkylated malononitriles. The dialkylated product was usually less polar.

2-Cyanopent-4-enenitrile (5a); 2-Cyano-2-(1-propenyl)-pent-4-enenitrile (4a).

These compounds were prepared by the general procedure for alkylation of malononitrile with allyl bromide (7.33g, 60.55 mmol), malononitrile (2.00g, 30.27 mmol), and LiH (0.28g, 35.22 mmol) in THF (80 mL). Chromatography of the crude product (silica gel, 10% EtOAc in hexanes) afforded **5a** (1.90g, 59%) and **4a** in a ratio of 4:3 as clear liquids: **5a** ^{1}H NMR ($CDCl_3$) δ 5.86 (1H, m), 5.42 (2H, m), 3.77 (1H, t, J = 6.6 Hz), 2.76 (2H, dd, J = 6.6, 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 129.15 (d), 122.00 (t), 112.35 (s), 34.22 (t), 22.70 (d); IR (thin film) 3090, 3025, 2960, 2930, 2860, 2260, 1420, 910, 740 cm^{-1}; **4a** ^{1}H NMR ($CDCl_3$) δ 5.89 (2H, m), 5.44 (4H, m), 2.68 (4H, d, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 128.39 (d), 123.02 (t), 114.72 (s), 40.50 (t), 37.13 (s); IR (thin film) 3090, 3020, 2990, 2930, 2270, 1660, 1460, 1430, 1320, 990, 930 cm^{-1}; LRMS (*m/e*) 145 ($M^+ - 1$), 119, 105, 81, 79, 68.

2-Cyanohex-4-enenitrile (5b); 2-Cyano-2-(2-butenyl)-hex-4-enenitrile (4b).

These compounds were prepared by the general procedure for alkylation of malononitrile with crotyl bromide (2.01 g, 14.90 mmol), malononitrile (0.82 g, 12.41 mmol), and LiH (108 mg, 13.65 mmol) in THF (40 mL). Chromatography of the crude product (silica gel, 10% EtOAc in hexanes) gave **5b** (0.94 g, 63%) and **4b** in a ratio of 3:1 as clear liquids: **5b** ^{1}H NMR ($CDCl_3$) δ 5.82 (1H, m), 5.49 (1H, m), 3.70 (1H, t, J = 6.6 Hz), 2.68 (2H, dd, J = 6.6, 6.8 Hz), 1.76 (3H, dd, J = 1.0, 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 134.02 (d), 121.82 (d), 112.37 (s), 33.98 (t), 23.55 (d), 18.02 (q); IR (thin film) 3040, 2975, 2925, 2870, 2260, 1460, 970 cm^{-1}; **4b** ^{1}H NMR ($CDCl_3$) δ 5.78 (2H, m), 5.52 (2H, m), 2.56 (4H, d, J = 7.3 Hz), 1.75 (6H, d, J = 6.4 Hz).

2-Cyano-2-(2-cyclopentenyl)ethanenitrile (5c); 2-Cyano-2,2-di-(2-cyclopentenyl)ethanenitrile (4c).

To a solution of 2-cyclopenten-1-yl acetate (2.27 g, 18.0 mmol) and bis-[1,2-bis(diphenyl phosphino)ethano]palladium [$Pd(dppe)_2$] (163 mg, 0.18 mmol) in THF (60 mL) was added lithiomalononitrile anion [prepared with malononitrile (2.38 g, 36.0 mmol) and lithium hydride (0.21 g, 27.0 mmol) in THF (60 mL)]. After heating at reflux for 4 h, the reaction mixture was diluted with ether (150 mL) and filtered through Florisil. The filtrate was washed with water (2 x 150 mL) and brine (150 mL), and concentrated under reduced pressure. The crude product was purified by flash column chromatography (12% EtoAc in hexanes) to afford dinitriles **5c** (1.53 g, 63%) and **4c** in a ratio of 8:1 as clear liquids: **5c** ^{1}H NMR ($CDCl_3$) δ 6.14 (1H, m), 5.63 (1H, m), 3.67 (1H, d, J = 6.2 Hz), 3.38 (1H, m), 2.60 (1H, m), 2.46 (1H, m), 2.35 (1H, m), 1.85 (1H, m); ^{13}C NMR ($CDCl_3$) δ 137.58 (d), 127.58 (d), 112.31 (s), 112.25 (s), 47.39 (d), 32.09 (t), 28.04 (d), 27.20 (t); IR (thin film) 3080, 2910, 2870, 2260, 1470, 1440, 1370, 990, 740 cm^{-1}; LRMS (*m/e*) 132 (M^+), 104, 90, 76, 67; **4c** ^{1}H NMR ($CDCl_3$) δ 6.16 (2H, m), 5.76 (2H, m), 3.30 (2H, m), 2.63 (2H, m), 2.42 (2H, m), 2.29 (2H, m), 1.98 (2H, m); ^{13}C NMR ($CDCl_3$) δ 137.68 (d), 126.64 (d),

114.97 (s), 51.24 (d), 32.14 (t), 29.69 (t), 26.48 (t); IR (thin film) 3070, 2930, 2860, 2250, 1620, 1470, 1440, 1370, 910 cm^{-1}; LRMS (*m/e*) 198 (M^+), 172, 132, 104, 67.

General Procedure for Preparation of α-Iodomalononitriles

Oil free sodium hydride (1.5 mmol) and *N*-iodosuccinimide (NIS, 1.8 mmol) were suspended in dry THF (20 mL). The malononitrile (1.0 mmol) in THF (10 mL) was slowly added to the suspension at 0 °C, and the mixture was stirred for 1 h at 0 °C in the dark. The resulting mixture was diluted with ether (2x), filtered through the silica gel pad, and concentrated under reduced pressure to give the crude iodide. This was purified by flash column chromatography to give the corresponding iodomalononitrile as a dark yellow oil.

2-Iodo-2-cyanopent-4-enenitrile (6a), (82%, 8% EtOAc in hexanes).
^1H NMR ($CDCl_3$) δ 5.87 (1H, m), 5.53 (2H, m), 3.05 (2H, d, J = 7.5 Hz); IR (thin film) 3070, 2980, 2940, 2870, 2360, 2250, 1090, 1020, 960 cm^{-1}.

2-Iodo-2-cyanohex-4-enenitrile (6b), (87%, 8% EtOAc in hexanes).
^1H NMR ($CDCl_3$) δ 5.91 (1H, m), 5.53 (1H, m), 2.97 (2H, m, J = 7.6, 3.7 Hz); ^{13}C NMR ($CDCl_3$) δ 136.32 (d), 122.25 (d), 114.02 (s), 46.38 (t), 22.94 (s), 18.11 (q).

2-Iodo-2-cyano-2-(2-cyclopentenyl)ethanenitrile (6c), (85%, 8% EtOAc in hexanes).
^1H NMR ($CDCl_3$) δ 6.22 (1H, m), 5.76 (1H, m), 2.64 (1H, m), 2.46 (1H, m), 2.32 (1H, m), 1.92 (1H, m).

General Procedure for forming adducts in Table 1: see preceding paper.[4]

4,4-Dicyano-6-iodo-1-decene (7).

Compound **7** was prepared with using iodomalononitrile **6a** (100 mg, 0.43 mmol) and 1-hexene (108 μL, 0.85 mmol) in benzene (1.5 mL). The reaction mixture was heated for 20 h at 80 °C, and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (6% EtOAc in hexanes) to give **7** (125 mg, 92%) as a clear oil: ^1H NMR ($CDCl_3$) δ 5.89 (1H, m), 5.45 (2H, m), 4.31 (1H, m), 2.73 (2H, d, J = 7.2 Hz), 2.66 (1H, dd, J = 6.5, 14.8 Hz), 2.54 (1H, dd, J = 7.7, 14.8 Hz), 1.87 (2H, m), 1.56 (1H, m), 1.50-1.28 (3H, m), 0.93 (3H, t); ^{13}C NMR ($CDCl_3$) δ 127.95 (d), 123.96 (t), 114.90 (s), 114.19 (s), 46.38 (t), 42.80 (t), 39.21 (t), 37.13 (s), 31.62 (t), 26.58 (d), 21.61 (t), 13.90 (q); LRMS (*m/e*) 189 ($M^+ \cdot - I$), 147, 133, 120, 107, 96, 81, 69, 55; HRMS calcd for $C_{12}H_{17}N_2$, 189.1392, found, 189.1391.

(3,4-*cis* and *trans*)-(2,3-*trans*)-1,1-Dicyano-4-iodomethyl-2-methyl-3-phenyl-cyclopentane (8 and 9).

Compounds **8** and **9** were prepared with iodomalononitrile **6a** (150 mg, 0.65 mmol) and β-methylstyrene (126 μL, 0.98 mmol) in benzene (2.2 mL). After heating for 3 days at 80 °C, purification by flash column chromatography (8% EtOAc in hexanes) gave cyclic iodides **8** and **9** (221 mg, 97% combined yield, in 2.4:1.0 ratio) as white solids: **8** (mp 129-130 °C); ^1H NMR ($CDCl_3$) δ 7.38 (3H, m), 7.12 (2H, d, J = 6.8 Hz), 3.18 (1H, dd, J = 10.0, 11.7 Hz), 3.08 (2H, m), 3.01 (1H, m), 2.89 (1H, dq, J = 6.6, 12.0 Hz), 2.65 (2H, d, J = 7.7 Hz), 2.23 (1H, dd, J = 8.3, 13.4 Hz), 1.29 (3H, d, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 135.48 (s), 129.14 (d), 128.04 (d), 127.20 (d), 115.46 (s), 114.16 (s), 55.25 (d), 49.11 (t), 45.52 (d), 42.87 (d), 39.31 (s), 14.32 (q), 8.25 (t); **9** mp 101-102 °C; ^1H NMR ($CDCl_3$) δ 7.36 (3H, m), 7.18 (2H, m), 3.22 (1H, dd, J = 3.4, 10.3 Hz), 3.05 (1H, dd, J = 7.5, 10.3 Hz), 2.87 (1H, dd, J = 9.3, 14.3 Hz), 2.78 (1H, dq, J = 6.9, 12.3 Hz), 2.60 (1H, dd, J = 10.3, 12.3 Hz), 2.53 (1H, d, J = 14.3 Hz), 2.44 (1H, m), 1.21 (3H, d, J = 6.9 Hz).

4,4-Dicyano-6-iodo-5,7-dimethyl-1-octenes (10a,b); (2,3-*ciss*)-(3,4-*cis*)-1,1-Dicyano-3-isopropyl-4-iodomethyl-2-methyl-cyclopentanes (11).

These compounds were prepared with iodomalononitrile **6a** (100 mg, 0.43 mmol) and cis-methyl-2-pentene (109 μL, 0.86 mmol) in benzene (1.5 mL). After heating for 3 d at 80 °C, chromatography of the crude product (10% EtOAc in hexanes) provided diastereomeric iodides **10a,b** (in a 3.3:1.0 ratio), accompanied by cyclic iodide **11** as slightly yellow oils. The combined yield was 65% (88 mg). The highest R_f value was **11** and the lowest was **10a**: **10a** ^1H NMR ($CDCl_3$) δ 5.92 (1H, m), 5.44 (2H, m), 4.22 (1H, dd, J = 7.0, 1.3 Hz), 2.82 (1H, dd, J = 13.8, 6.9 Hz), 2.68 (1H, dd, J = 13.8, 7.5 Hz), 1.86 (1H, dt, J = 7.0, 6.6 Hz), 1.74 (1H, m), 1.34 (3H, d, J = 6.6 Hz), 1.14 (3H, d, J = 6.5 Hz), 1.01 (3H, d, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 128.59 (d), 123.63 (t), 114.51 (s), 114.26 (s), 47.14 (d), 43.89 (s), 40.86 (t), 40.24 (d), 35.94 (d), 24.10 (d), 20.70 (q), 16.16 (q); **10b** ^1H NMR ($CDCl_3$) δ 5.92 (1H, m), 5.46 (2H, m), 4.86 (1H, dd, J = 2.2, 4.0 Hz), 2.84 (1H, dd, J = 13.8, 6.9 Hz), 2.66 (1H, dd, J = 13.8, 7.7

Hz), 2.57 (1H, dq, J = 4.0, 7.2 Hz), 1.51 (3H, d, J = 7.2 Hz), 1.02 (3H, d, J = 6.2 Hz), 1.00 (3H, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 128.23 (d), 123.90 (t), 114.61 (s), 114.39 (s), 48.55 (d), 47.00 (d), 44.45 (s), 41.50 (t), 30.50 (d), 25.84 (d), 23.13 (q), 14.68 (q); **11** ^{1}H NMR ($CDCl_3$) δ 3.44 (1H, dd, J = 4.9, 7.9 Hz), 3.09 (1H, dd, J = 10.4, 10.0 Hz), 2.86-2.74 (2H, m), 2.53 (1H, m), 2.00 (1H, m), 1.82 (1H, m), 1.41 (3H, d, J = 6.7 Hz), 1.20 (1H, m), 1.01 (3H, d, J = 6.7 Hz), 0.99 (3H, d, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 116.39, 114.77, 52.79, 45.90, 44.74, 44.31, 43.21, 26.94, 22.89, 20.32, 17.56, 6.21.

***trans*-1-Allyldicyanomethyl-2-iodo-cyclopentane (12a).**

Compound **12a** was prepared with iodomalononitrile **6a** (100 mg, 0.43 mmol) and cyclopentene (76 μL, 0.85 mmol) in benzene (1.5 mL). After heating for 23 h at 80 °C, purification by flash column chromatography (6% EtOAc in hexanes) afforded **12a** (92 mg, 71%) as a clear oil: ^{1}H NMR ($CDCl_3$) δ 5.92 (1H, m), 5.44 (2H, m), 4.28 (1H, dt, J = 4.8, 6.9 Hz), 2.94 (1H, dt, J = 4.8, 8.4 Hz), 2.75 (2H, d, J = 7.4 Hz), 2.26 (2H, m), 2.15 (1H, m), 2.01-1.83 (2H, m), 1.72 (1H, m); ^{13}CNMR ($CDCl_3$) δ 128.49 (d), 123.61 (t), 114.33 (s), 114.16 (s), 56.40 (d), 42.71 (s), 41.38 (t), 40.53 (t), 30.53 (t), 25.53 (t), 25.20 (t), 21.70 (d); LRMS (*m/e*) 300 (M^+), 227, 195, 173, 107, 94, 67; HRMS calcd for $C_{11}H_{13}N_2I$, 300.0123, found, 300.0123.

2-Cyano-2-(2-iodocyclopentyl)-hex-4-enenitrile (12b).

Iodide **12b** was prepared with iodomalononitrile **6b** (300 mg, 1.21 mmol) and cyclopentene (215 μL, 2.45 mmol) in benzene. The addition reaction was performed with an iodide concentration of 0.3M to give **12b** (311 mg, 82%) as a yellow liquid: ^{1}H NMR ($CDCl_3$) δ 5.88 (1H, m), 5.54 (1H, m), 4.29 (1H, dt, J = 6.8, 4.9 Hz), 2.94 (1H, dt, J = 8.6, 4.9 Hz), 2.69 (2H, dd, J = 7.4, 3.5 Hz), 2.26 (2H, m), 2.14 (1H, m), 1.90 (2H, m), 1.89 (3H, d, J = 6.4 Hz), 1.71 (1H, m); ^{13}C NMR ($CDCl_3$) δ 134.86 (d), 121.05 (d), 114.52 (s), 114.52 (s), 114.39 (s), 56.22 (d), 43.22 (s), 41.32 (t), 39.62 (t), 30.47 (t), 25.17 (t), 21.90 (d), 18.11 (q).

***trans*-1-[(2-Cyclopentenyl)dicyanomethyl]-2-iodo-pentanes (13a/b).**

A solution of iodomalononitrile **6c** (0.20 g, 0.78 mmol) and cyclopentene (137 μL, 1.56 mmol) in benzene (4 mL) was heated for 24 h at 80 °C under dark. After evaporation of the solvent, the residue was purified by flash column chromatography (8% EtOAc in hexanes) to give an unassigned 1:1 mixture of **13a** and **13b** (0.12 g, 48% combined yield) as a yellow solid: **13a** ^{1}H NMR ($CDCl_3$) δ 6.17 (1H, m), 5.74 (1H, m), 4.30 (1H, m), 3.44 (1H,m), 2.98 (1H, m), 2.62 (1H, m), 2.46 (1H, m), 2.36 (1H, m), 2.28 (2H, m), 2.15 (1H, m), 1.92 (3H, m), 1.74 (1H, m); ^{13}C NMR ($CDCl_3$) δ 138.20 (d), 126.40 (d), 114.39 (s), 55.15 (d), 51.38 (d), 48.02 (s), 41.52 (t), 32.25 (t), 31.06 (t), 26.24 (t), 25.21 (t), 22.11 (d); **13b** ^{1}H NMR ($CDCl_3$) δ 6.17 (1H, m), 5.79 (1H, m); ^{13}C NMR ($CDCl_3$) δ 138.22 (d), 127.01 (d), 114.39 (s), 55.17 (d), 51.40 (d), 48.14 (s), 41.52 (t), 32.25 (t), 31.14 (t), 26.35 (t), 25.21 (t), 22.24 (d).

***trans* and *cis*-1-Allyldicyanomethyl-2-iodocyclohexane (14-trans & cis).**

The compound **14** was prepared with iodomalononitrile **6a** (100 mg, 0.43 mmol) and cyclohexene (88 μL, 0.86 mmol) in benzene (1.5 mL). After heating for 24 h at 80 °C, purification by flash column chromatography (10% EtOAc in hexanes) provided iodides **14-trans** and **14-cis** (50 mg, 37% combined yield, in a 2.0:1.0 ratio) as slightly yellow oils: **14-trans** ^{1}H NMR ($CDCl_3$) δ 5.93 (1H, m), 5.46 (2H, m), 4.45 (1H, dt, J = 8.6, 3.4 Hz), 2.90 (2H, d, J = 7.2 Hz), 2.50 (1H, m), 2.37 (1H, m), 2.26 (1H, m), 2.13 (1H, m), 1.96 (1H, m), 1.62 (1H, m), 1.51 (2H, m); ^{13}C NMR ($CDCl_3$) δ 128.59 (d), 126.02 (t), 115.14 (s), 114.81 (s), 48.04 (d), 42.60 (s), 40.54 (t), 38.89 (t), 28.28 (t), 27.80 (t), 25.91 (t), 23.33 (d); **14-cis** ^{1}H NMR ($CDCl_3$) δ 5.94 (1H, m), 5.44 (2H, m), 4.74 (1H, dt, J = 2.9, 1.7 Hz), 2.83 (1H, dd, J = 13.1, 6.9 Hz), 2.72 (1H, dd, J = 13.1, 7.5 Hz), 2.26 (1H, dt, J = 10.8, 1.7 Hz), 1.98-1.73 (5H, m), 1.68 (1H, m), 1.40 (1H, m), 1.26 (1H, m).

General Procedure for the Nitrile Transfer Cyclizations.

A solution of iodides (1.0 equiv), tributyltin hydride (1.1 equiv), and AIBN (10 mole%) in dry benzene (0.1-0.2 M) was refluxed for 3-8 h. The resulting mixture was diluted with ether (4x), treated with 1.5 equiv of DBU, and eluted through silica gel pad (5 cm length; eluent was Et_2O). The filtrate was condensed under reduced pressure. The crude product was purified by column chromatography (two sequential elutions separation with eluents having different polarity) to give the general dinitrile followed by the nitrile transfer products.

(1,4-*cis and trans*)-(3,4-*cis*)-1-Cyano-4-cyanomethyl-3-butylcyclopentanes (cis and trans).

Preparation followed the general procedure with iodide **7** (135 mg, 0.46 mmol), Bu_3SnH (136 μL, 0.50 mmol), and AIBN (8 mg) in benzene (3.0 mL). DBU work up and purification by MPLC (10% EtOAc in hexanes) afforded an

inseparable 2.90:1 mixture of **15a,b** (72 mg, 82% combined yield) as a clear liquid: **15a** ^{1}H NMR ($CDCl_3$) δ 2.83 (1H, m), 2.49-2.34 (3H, m), 2.32-2.22 (2H, m), 2.05 (1H, m), 1.89 (1H, m), 1.72 (1H, m), 1.46-1.22 (4H, m), 0.91 (3H, t , J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 122.77 (s), 118.89 (s), 41.89 (d), 38.89 (d), 35.84 (t), 35.39 (t), 30.34 (t), 29.02 (t) 25.56 (d), 22.75 (t), 18.38 (t), 14.01 (q); **15b** ^{1}H NMR ($CDCl_3$) δ 3.02 (1H, m), 2.56 (1H, m), 2.39 (1H, m), 2.32-2.19 (2H, m), 2.16 (1H, m), 2.07 (1H, m), 1.84 (1H, m), 1.42-1.14 (5H, m), 0.93 (3H, t); ^{13}C NMR ($CDCl_3$) δ 123.08 (s), 118.88 (s), 41.59 (d), 38.36 (d), 35.71 (t), 35.07 (t), 30.40 (t), 28.75 (t), 25.58 (d), 25.77 (t), 17.83 (t), 14.01 (q); IR (thin film) (**mixture**) 2960, 2930, 2870, 2240, 1470, 1430, 1380, 740 cm^{-1}; LRMS (*m/e*) 189 ($M^+ - 1$), 175, 162, 148, 122, 108, 94, 81, 67; HRMS calcd for $C_{12}H_{17}N_2$, 189.1392, found, 189.1392.

(1,4-*cis and trans*)-(2,3-*trans*)-(3,4-*cis*)-1-Cyano-4-cyanomethyl-2-methyl-3-isopropylcyclopentane (20a,b); (3,4-*cis and trans*)-(2,3-*trans*)-1,1-Dicyano-2,4-dimethyl-3-isopropylcyclopentane (21a,b).

Preparation followed the general procedure with the iodides **10a,b** (249 mg, 0.79 mmol), Bu_3SnH (233 μL, 0.87 mmol) and AIBN (15 mg) in benzene (8.0 mL). DBU work up and purification by flash column chromatography (100% hexanes and 15% EtOAc in hexanes) gave an inseparable mixture of **20a,b** (72 mg, 48%, in 5.26:1 ratio on GC), along with an inseparable mixture of **21a,b** (5 mg, 3%): **20a,b (mixture)** ^{1}H NMR ($CDCl_3$) δ 3.11 (1H, dt, J = 8.4, 8.9 Hz, assigned to cis isomer), 2.84 (1H, dt, J = 9.2, 8.3 Hz, assigned to trans isomer), 2.62-2.35 (3H, m), 2.31-2.18 (2H, m), 2.17-2.02 (4H, m), 1.94 (2H, m), 1.76 (2H, m), 1.53 (3H, m), 1.25 (3H, d, J = 7.0 Hz, assigned to trans isomer), 1.21 (3H, d, J = 6.9 Hz, assigned to cis isomer), 0.96-0.87 (12H, m); ^{13}C NMR ($CDCl_3$) **20a** δ 120.59 (s), 118.88 (s), 55.61 (d), 38.26 (d), 35.74 (d), 35.16 (t), 32.89 (d), 28.26 (d), 22.29 (q), 21.28 (q), 19.99 (q), 17.76 (t); IR (thin film) 2970, 2930, 2880, 2240, 1470, 1430, 1390, 1010 cm^{-1}; LRMS (*m/e*) 190 (M^+), 189 ($M^+ - 1$), 175, 150, 134, 122, 108, 83, 68; HRMS calcd for $C_{12}H_{18}N_2$, 190.1470, found, 190.1470; **21a,b** ^{1}H NMR ($CDCl_3$) δ 2.83-2.60 (2H, m), 2.48-2.28 (2H, m), 2.16-1.94 (4H, m), 1.83-1.62 (4H, m), 1.38 (3H, d, J = 6.4 Hz, trans isomer), 1.28 (3H, d, J = 6.4 Hz, cis isomer), 1.24 (3H, d, J = 6.7 Hz, trans isomer), 1.18 (3H, d, J = 6.7 Hz, cis isomer), 1.08 (6H, d, J = 6.7 Hz, trans isomer), 0.98 (6H, d, J = 6.8 Hz, cis isomer); IR (thin film) 2960, 2930, 2880, 2250, 1470, 1390, 940 cm^{-1}; LRMS (*m/e*) 190 (M^+), 189 ($M^+ - 1$), 162, 147, 120, 106, 79, 69.

(1,4-*cis and trans*)-(2,3-*trans*)-(3,4-*cis*)-1-Cyano-4-cyanomethyl-2-methyl-3-phenyl-cyclopentane (22a,b); (2,3-*trans*)-(3,4-*cis*)-1,1-Dicyano-2,4-dimethyl-3-phenyl-cyclopentane (23).

Preparation followed the general procedure with iodide **8** (867 mg, 2.50 mmol), Bu_3SnH (741 μL, 2.75 mmol), and AIBN (45 mg) in benzene (17.0 mL). DBU workup and purification by flash column chromatography (4% and 10% EtOAc in hexanes) gave a partially separable mixture of cyclopentanes **22a** and **22b** (322 mg, 66%, in 1.08:1 ratio), along with **23** (104 mg, 21%) as clear liquids: **22a** ^{1}H NMR ($CDCl_3$) δ 7.34 (3H, m), 7.15 (2H, m), 3.18 (1H, dd, J = 9.6, 11.5 Hz), 2.94 (1H, dd, J = 9.6, 9.2 Hz), 2.70-2.48 (3H, m), 2.00 (1H, m), 1.98-1.84 (2H, m), 1.17 (3H, d, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 137.04, (s), 128.74 (d), 127.38 (d), 127.31 (d), 121.16 (s), 118.56 (s), 54.37 (d), 53.31 (d), 42.63 (d), 38.56 (d), 38.20 (d), 35.23 (t), 34.82 (d), 20.37 (t), 16.92 (q); **22b** ^{1}H NMR ($CDCl_3$) δ 3.27 (1H, dt, J = 7.6, 2.1 Hz), 2.81 (1H, m), 2.07 (1H, m) 1.14 (3H, d, J = 6.7 Hz) (other peaks were overlapped with the corresponding peaks of **22a**); ^{13}C NMR ($CDCl_3$) δ 128.34 (d) 120.45 (s), 118.60 (s), 38.97 (d), 35.01 (t), 34.32 (d), 20.02 (t), 15.46 (q) (other peaks were overlapped with the corresponding peaks of **22a**); IR (thin film, mixture) 3062, 3031, 2964, 2930, 2876, 2239, 1602, 1470, 1422, 1080, 740, 704 cm^{-1}; LRMS (*m/e*) 224 (M^+), 209, 182, 167, 146, 131, 117, 105, 91, 78, 65; **23** ^{1}H NMR ($CDCl_3$) δ 7.32 (3H, m), 7.10 (2H, d, J = 7.1 Hz), 3.13 (1H, dd, J = 9.8, 11.6 Hz), 2.86 (2H, m), 2.67 (1H, dq, J = 7.5, 9.8 Hz), 2.10 (1H, dd, J = 7.9, 13.5 Hz), 1.28 (3H, d, J = 6.6 Hz), 0.66 (3H, d, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 137.45 (s), 128.72 (d), 128.63 (d), 127.26 (d), 116.27 (s), 114.80 (s), 53.40 (d), 48.55 (d), 45.48 (t), 39.73 (s), 35.06 (d), 17.89 (q), 14.27 (q); IR (thin film) 3063, 3030, 2970, 2932, 2876, 2248, 1602, 1454, 1384, 748, 702 cm^{-1}; LRMS (*m/e*) 224 (M^+), 209, 182, 167, 146, 131, 117, 105, 91, 78, 65; HRMS calcd for $C_{15}H_{16}N_2$ 224.1287, found 224.1287.

(1,4-*cis and trans*)-(2,3-*trans*)-(3,4-*trans*)-1-Cyano-4-cyanomethyl-2-methyl-3-phenylcyclopentane (24a,b); (2,3-*trans*)-(3,4-*trans*)-1,1-Dicyano-2,4-dimethyl-3-phenyl-cyclopentane (25).

Preparation followed the general procedure with iodide **9** (326 mg, 0.93 mmol), Bu_3SnH (276 μL, 1.02 mmol), and AIBN (17 mg) in benzene (6.0 mL). DBU workup and purification by flash column chromatography (4% and 10% EtOAc in hexanes) gave cyclopentanes **24a,b** (92 mg, 44%, in 1.46:1 ratio), along with **25f** (71 mg, 34%) as clear liquids: **24a** ^{1}H NMR ($CDCl_3$) δ 7.32 (3H, m), 7.14 (2H, m), 2.62 (1H, dt, J = 6.5, 9.8 Hz), 2.52-2.34 (4H, m) 2.32-2.14 (2H, m), 2.13 (1H, m), 1.03 (3H, d, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ 138.36 (s), 129.20 (d), 127.84 (d), 127.59 (d), 121.89 (s), 117.67 (s), 58.42 (d), 47.51 (d), 42.31 (d), 34.03 (t), 33.40 (t), 20.41 (t), 16.75 (q); **24b** ^{1}H

NMR ($CDCl_3$) δ 7.34 (3H, m), 7.16 (2H, m), 3.22 (1H, m, J = 6.1, 7.4, 8.2 Hz), 2.64 (1H, dt, J = 7.7, 13.0 Hz), 2.46-2.24 (5H, m), 2.03 (1H, m), 1.11 (3H, d, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 138.72 (s), 129.56 (d), 127.36 (d), 126.80 (d), 120.76 (s), 117.82 (s), 58.12 (d), 43.92 (d), 43.09 (d), 33.70 (t), 33.38 (t), 20.85 (t), 14.71 (q); IR (thin film, mixture) 3060, 3030, 2930, 2870, 2240, 1600, 1455, 1420, 760, 700 cm^{-1}; LRMS (*m/e*) 224 (M^+), 209, 182, 167, 146, 131, 117, 105, 91, 78, 65; **25** ^1H NMR ($CDCl_3$) δ 7.36 (3H, m), 7.21 (2H, m), 2.88 (1H, dd, J = 8.2, 13.6 Hz), 2.67 (1H, m), 2.44-2.66 (2H, m), 1.76 (1H, m), 1.22 (3H, d, J = 6.7 Hz), 1.05 (3H, d, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 138.65 (s), 129.04 (d), 127.66 (d), 126.82 (d), 116.78 (s), 115.38 (s), 52.46 (d), 44.70 (t), 40.56 (d), 38.56 (s), 33.08 (d), 18.53 (q), 14.33 (q); IR (thin film) 3070, 3030, 2970, 2930, 2870, 2250, 1660, 1460, 1430, 760, 710 cm^{-1}; LRMS (*m/e*) 224 (M^+), 209, 182, 168, 146, 117, 105, 92, 78, 65.

***cis*-(1,3-*cis*)-1-Cyano-27-cyanomethylbicyclo[3.3.0]octane (26a); *cis*-1,1-Dicyano-3α-methylbicyclo[3.3.0]octane (27).**

Preparation of **26a** followed the general procedure with iodide **12a** (100 mg, 0.33 mmol), Bu_3SnH (99 μL, 0.37 mmol) and AIBN (6 mg) in benzene (3.0 mL). DBU workup and purification by MPLC (2% and 15% EtOAc in hexanes) gave **26a** (40 mg, 69.6%) and **27** (9.5 mg, 16.5%) as clear liquids: **26a** ^1H NMR ($CDCl_3$) δ 2.83 (2H, m), 2.66 (1H, m), 2.50-2.36 (2H, m), 2.52-2.15 (2H, m), 2.08 (1H, m), 1.81 (2H, m), 1.68-1.54 (1H, m), 1.53-1.34 (2H, m), 1.18 (1H, m); ^{13}C NMR ($CDCl_3$) δ 120.30 (s), 118.59 (s), 45.51 (d), 44.12 (d), 38.76 (d), 34.06 (t), 32.06 (t), 32.15 (d), 31.80 (t), 27.90 (t), 27.11 (t), 18.01 (t); IR (thin film) 2970, 2870, 2245, 1460, 1390, 1090, 920, 800, 690 cm^{-1}; LRMS (*m/e*) 173 ($M^+ - 1$) 156, 146, 134, 121, 107, 94, 80, 67; HRMS calcd for $C_{11}H_{14}N_2$, 173.1076, found, 173.1017; **27** ^1H NMR ($CDCl_3$) δ 3.04 (1H, q, J = 8.3 Hz), 2.63 (1H, m), 2.46 (1H, m), 2.36 (1H, m), 2.16 (1H, m), 1.82 (1H, dd, J = 12.8, 12.8 Hz), 1.74 (2H, m), 1.44 (2H, m), 1.28 (1H, m), 1.06 (3H, d, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$) δ 117.45 (s), 115.22 (s), 53.14 (d), 46.54 (d), 42.79 (t), 37.96 (s), 35.07 (d), 32.38 (t), 27.73 (t), 26.85 (t), 13.83 (q); IR (thin film) 2980, 2870, 2250, 1470, 1390, 1170, 920 cm^{-1}; LRMS (*m/e*) 174 (M^+), 159, 145, 133, 120, 105, 96, 81, 67; HRMS calcd for $C_{11}H_{14}N_2$, 174.1154, found, 174.1155.

***cis*-(1,3-*cis and trans*)-1-Cyano-3-cyanomethylbicyclo[4.3.0]nonanes (28a,b); 3α- & 3β-Methyl-1,1-dicyano-bicyclo[4.3.0]nonanes (29a,b).**

Preparation followed the general procedure with iodide **14** (150 mg, 0.48 mmol), Bu_3SnH (142 μL, 0.53 mmol) and AIBN (9 mg) in benzene (4.8 mL). DBU workup and purification by flash column chromatography (2% and 20% EtOAc in hexanes) provided an inseparable mixture of **28a,b** (49 mg, 55.2%, in 14.3:1 ratio on GC), along with the mixture of **29a.b** (11.5 mg, 12.8%) as clear liquids: **28** ^1H NMR ($CDCl_3$) δ 3.08 (1H, dt, J = 8.6, 9.3 Hz), 2.47 (1H, m), 2.42 (2H, m), 2.32 (2H, m), 2.08 (1H, m), 1.92-1.70 (5H, m), 1.59 (2H, m), 1.21 (1H, m), 1.12 (1H, m); ^{13}C NMR ($CDCl_3$) δ 122.76 (s), 118.65 (s), 41.67 (d), 39.89 (d), 39.72 (d), 34.97 (t), 29.47 (d), 25.17 (t), 23.75 (t), 22.13 (t), 21.28 (t), 18.01 (t); IR (thin film) 2940, 2860, 2230, 1460, 1430, 1370, 920, 760 cm^{-1}; LRMS (*m/e*) 188 (M^+), 187 ($M^+ - 1$), 173, 160, 148, 135, 120, 108, 94, 79, 67; HRMS calcd for $C_{12}H_{16}N_2$ 188.1330, found 188.1330; **29a** ^1H NMR ($CDCl_3$) δ 2.83 (1H, dd, J = 8.4, 16.4 Hz), 2.70 (1H, m), 2.68 (1H, dd, J = 7.3, 16.4 Hz), 2.36 (1H, m), 2.12 (1H, m), 1.96-1.70 (3H, m), 1.58 (1H, m), 1.23 (4H, m), 1.03 (3H, d, J = 6.8 Hz); **29b** ^1H NMR ($CDCl_3$) δ 2.53 (1H, m), 1.09 (3H, d, J = 6.5 Hz); IR (thin film) 2940, 2870, 2250, 1460, 940 cm^{-1}; LRMS (*m/e*) 188 (M^+), 174, 160, 146, 110, 95, 79, 68.

***cis*-(1,3-cis)-1-Cyano-3-(2-cyanoethyl)bicyclo[3.3.0]octane; (30) *cis*-1,1-Dicyano-3α-ethylbicyclo[3.3.0]octane (31).**

The cyclization of iodide **12b** (310 mg, 0.99 mmol) was conducted at a concentration of 0.1M (in benzene) by use of Bu_3SnH (293 μL, 1.08 mmol) and a catalytic amount of AIBN (18 mg). Isomers **31** and **30** (1:20 ratio) were obtained in a combined yield of 78% (146 mg) after purification by flash column chromatography (silica gel, 2% and 15% EtOAc in hexanes): **30** ^1H NMR ($CDCl_3$) δ 2.81 (1H, m), 2.79 (1H, m), 2.54 (2H, m), 2.34 (1H, dt, J = 6.0, 12.3 Hz), 2.02 (2H, m), 1.81 (1H, m), 1.72 (2H, m), 1.49 (1H, m), 1.38 (3H, d, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 122.25 (s), 120.30 (s), 45.87 (d), 44.05 (d), 44.04 (d), 33.35 (t), 31.76 (d), 31.75 (t), 27.34 (t), 26.95 (t), 26.38 (d), 17.27 (q); IR (thin film) 2960, 2870, 2250, 1460, 1400, 1110, 790 cm^{-1}; LRMS (*m/e*) 187 ($M^+ - 1$), 173, 160, 148, 134, 108, 93, 67; HRMS calcd for $C_{12}H_{15}N_2$ 187.1232, found, 187.1235; **31** ^1H NMR ($CDCl_3$) δ 3.06 (1H, q, J = 8.4 Hz), 2.68 (1H, m), 2.46 (1H, m), 2.38 (1H, m), 1.98 (1H, m), 1.78 (1H, t, J = 12.6 Hz), 1.72 (2H, m), 1.45 (4H, m), 1.26 (1H, m), 0.94 (3H, t); IR (thin film) 2970, 2940, 2880, 2860, 2240, 1470, 1390, 1100, 1090, 890 cm^{-1}; LRMS (*m/e*) 188 (M^+), 173, 162, 136, 110, 67.

(4,6,10,11-*cis/anti/cis*- & *cis/syn/cis*)-1,5-dicyanotricyclio[3.3.0.0]undecane (36 and 37).

The tin hydride cyclization of the mixture of **13** (0.12 g, 0.37 mmol) was conducted with Bu_3SnH (109 μL, 0.40 mmol) and catalytic AIBN (7 mg) in refluxing benzene (3.7 mL). After 12 h, the mixture was diluted with ether

(20 mL), treated with 1.5 equiv of DBU, and eluted through silica gel pad. The filtrate was concentrated on the rotary evaporator and purified by flash column chromatography (5% EtOAc in hexanes) to provide a partially separable mixture of four isomers **36/37** (64 mg, 87%) in the 1.9:1.5:1.0:0.3 ratio as clear oils: **The first major isomer** ^{1}H NMR ($CDCl_3$) δ 3.21 (1H, dd, J = 10.3, 10.1 Hz), 2.96 (2H, m), 2.81 (2H, m), 2.66 (1H, m), 2.25 (2H, m), 2.12 (1H, m), 2.04 (2H, m), 1.94 (2H, m), 1.82 (1H, m), 1.57 (2H, m); ^{13}C NMR ($CDCl_3$) δ 121.27 (s), 120.03 (s), 49.02 (d), 48.87 (d), 48.57 (d), 48.18 (d), 37.41 (d), 31.28 (t), 30.68 (t), 29.50 (t), 28.96 (t), 28.70 (t), 27.15 (t); **The second major isomer** ^{1}H NMR ($CDCl_3$) δ 2.84 (2H, m), 2.63 (1H, m), 2.48 (1H, m), 2.12-1.94 (2H, m), 1.92 (4H, m), 1.68-1.54 (4H, m), 1.42 (1H, m); ^{13}C NMR ($CDCl_3$) δ 120.96 (s), 120.86 (s), 53.31 (d), 49.43 (d), 47.85 (d), 39.63 (d), 35.13 (d), 33.74 (t), 33.00 (t), 30.23 (t), 27.92 (t), 24.94 (t).

2-Cyano-2-(2-cyclopentenyl)-4-bromo-pent-4-enenitrile (39a).

Sodium hydride (0.65 g, 13.5 mmol, 50% by weight oil dispersion) was placed in a tared, flame-dried 50 mL centrifuge tube and washed with dry hexanes (3 x 20 mL) to remove the oil. The oil-free sodium hydride was then purged with nitrogen and suspended in THF (30 mL). The centrifuge tube was placed on a magnetic stirring apparatus, and cooled to 0 °C. The malononitrile **5c** (1.49 g, 11.25 mmol) in THF (20 mL) was cautiously added to the stirred suspension. During this addition, gas evolution was observed. The mixture was allowed to stir for 15 min at room temperature, and then centrifuged. The supernatant solution was transferred to a dried flask via a cannula. A solution of 2,3-dibromo-1-propene (4.50 g, 22.50 mmol) in THF (20 mL) was added dropwise over 15 min to the anion solution at 0 °C. The mixture was allowed to stir for 3 h at 25°C, and then poured into ether/ice water mixture. The organic layer was washed with water (2 x 100 mL) and brine (100 mL), and dried over anhydrous $MgSO_4$. After evaporation of the solvent, flash column chromatography (6% EtOAc in hexanes) of the crude produced vinyl bromide **39a** (2.40 g, 85%) as a slightly yellow solid: ^{1}H NMR ($CDCl_3$) δ 6.19 (1H, m, J = 5.7, 4.5, 2.2 Hz), 6.00 (1H, d, J = 2.4 Hz), 5.84 (1H, d, J = 2.5 Hz), 5.74 (1H, ddd, J = 5.7, 4.5, 2.2 Hz), 3.41 (1H, m), 3.02 (2H, s), 2.62 (1H, m), 2.48 (1H, m), 2.32 (1H, m), 1.94 (1H, m); ^{13}C NMR ($CDCl_3$) δ 138.62 (d), 125.97 (d), 124.36 (t), 122.71 (s), 114.42 (s), 114.26 (s), 53.34 (d), 45.54 (t), 41.89 (s), 32.31 (t), 26.16 (t); IR (thin film) 3070, 3030, 2940, 2870, 2260, 1630, 1470, 1430, 1330, 1170, 1150, 920, 760 cm^{-1}; LRMS (*m/e*) 171 (M^+ – Br), 144, 130, 74, 67, 59; HRMS calcd for $C_{11}H_{11}N_2$ 171.0922 , found 171.0922.

2-Cyano-2-(2-cyclohexenyl)-4-bromo-pent-4-enenitrile (39b).

Vinyl bromide **39b** was prepared by the procedure given for **39a** with **38** (1.20 g, 8.05 mmol), 2,3-dibromo-1-propene (3.22 g, 16.10 mmol), and NaH (0.46 g, 9.66 mmol, 50% by weight oil dispersion) in THF (120 mL). Purification by flash column chromatography (6% EtOAc in hexanes) afforded vinyl bromide **39b** (1.79 g, 83%) as slightly yellow solids: ^{1}H NMR ($CDCl_3$) δ 6.13 (1H, m, J = 10.3, 6.4, 3.2 Hz), 6.00 (1H, d, J = 2.2 Hz), 5.84 (1H, d, J = 2.4 Hz), 5.69 (1H, m, J = 10.3, 1.8 Hz), 3.04 (2H, s), 2.84 (1H, m), 2.17-2.08 (3H, m), 1.95 (1H, m), 1.59 (2H, m); ^{13}C NMR ($CDCl_3$) δ 134.64 (d), 124.35 (t), 122.82 (s), 122.03 (d), 114.6 (s), 113.93 (s), 44.27 (t), 42.33 (d), 41.89 (s), 25.13 (t), 24.49 (t), 20.89 (t); IR (thin film) 3040, 2940, 2840, 2260, 1635, 1450, 1430, 1160, 910, 760, 740 cm^{-1}; LRMS (*m/e*) 185 (M^+ – Br), 144, 81, 67, 53; HRMS calcd for $C_{12}H_{13}N_2$ 185.1079, found 185.1079.

***cis*-3,6-Dicyano-1-(methylene)bicyclo[3.3.0]octane (42a).**

A solution of a vinyl bromide **39a** (0.70 g, 2.79 mmol) in dry benzene (5 mL) was added to a solution of Bu_3SnH (751 μL, 2.79 mmol) and AIBN (46 mg, 0.28 mmol) in dry benzene (2 mL), and the total volume was adjusted to give a 0.1 M solution of the radical precursor. The reaction mixture was refluxed for 10 h, and then evaporated under reduced pressure. The residue was dissolved in ether (100 mL) and treated with 1.5 equiv of DBU. The resulting mixture was filtered through a silica gel pad and concentrated. Purification by chromatography (15% EtOAc in hexanes) gave **41a** (0.13 g, 27%) and **42a** (0.28 g, 58%) as clear oils: **42a** ^{1}H NMR ($CDCl_3$) δ 5.27 (1H, m), 5.18 (1H, m), 3.18 (1H, m), 3.11 (1H, m), 2.96 (2H, m), 2.58 (2H, m), 2.08-1.99 (4H, m); ^{13}C NMR ($CDCl_3$) δ 146.02 (s), 120.03 (s), 119.72 (s), 113.04 (t), 49.20 (d), 44.68 (d), 37.72 (t), 36.10 (d), 31.88 (d), 31.62 (t), 29.12 (t); IR (thin film) 3090, 2970, 2890, 2240, 1670, 1460, 910 cm^{-1}; LRMS (*m/e*) 172 (M^+), 171, 157, 145, 130, 118, 104, 92, 79, 65, 54; HRMS calcd for $C_{11}H_{12}N_2$, 172.1000, found, 172.1000.

***cis*-3,7-Dicyano-1-(methylene)bicyclo[4.3.0]nonane (42b).**

Compounds **41b** and **42b** were prepared by the same procedure for **41a**, with **39b** (1.0 g, 3.73 mmol), Bu_3SnH (100 μL, 3.73 mmol) and AIBN (61 mg, 0.37 mmol) in benzene (37 mL). Purification by column chromatography (15% EtOAc in hexenes) afforded **41b** (0.10 g, 14%) and **42b** (0.48 g, 69%) as clear oils: **42b** ^{1}H NMR ($CDCl_3$) δ 5.58 (1H, m), 5.18 (1H, m), 2.96-2.78 (4H, m), 2.68 (1H, m), 2.26 (1H, m), 1.90-1.69 (4H, m), 1.27 (1H, m), 1.08 (1H, m); ^{13}C NMR ($CDCl_3$) δ 142.34 (s), 121.13 (s), 119.72 (s), 110.64 (t), 42.90 (d), 41.50 (d), 34.51 (t), 29.50 (d), 27.95 (d), 23.93 (t), 23.58 (t), 22.81 (t); IR (thin film) 3100, 2940, 2870, 2250, 1670,

1460, 900, 870 cm^{-1}; LRMS (*m/e*) 186 (M^+), 185 ($M^+ - 1$), 171, 159, 144, 132, 118, 106, 91, 77, 65, 51; HRMS calcd for $C_{12}H_{14}N_2$ 186.1313, found 186.1313.

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13. Another possibility is that the cyclization of **16** is not selective and gives a cis/trans mixture. However, we are then left with the unlikely proposition that the hydrogen abstraction reactions of these two radicals are highly selective.
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16. We estimate that k_C for the reaction **16** $\rightarrow$ **17** must exceed 10^5 s^{-1}.

17. There are: one directly reduced product, four cyclized products (5-exo) with no nitrile transfer, eight products of nitrile transfer, and two 6-endo products.

18. In fact, the cyclization must not be completely selective because traces of two epimers of **21** are detected.

19. Both the C1 nitrile carbon and the methyl carbon are shielded in the **b** series relative to the **a** series. See, Whitesell, J. K. and Minton, M. A. "Stereochemical Analysis of Alicyclic compounds by C-13 NMR Spectroscopy"; Chapman and Halle, London; 1987.

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25. The use of temporary rings to control stereochemistry is a common synthetic tactic. Usually, the rings are formed and cleaved in separate steps. This strategy has been extensively applied to radical cyclizations by Stork. Leading references: Stork, G.; Suh, H. S.; Kim, G. *J. Am. Chem. Soc.* **1991**, *113*, 7054. Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741.

26. Geminal dinitriles exhibit a characteristic singlet ~40 ppm in the ^{13}C NMR for the carbon bearing the nitriles. The ^{13}C NMR spectra of **36/37** exhibited no peaks in this region.

27. Products **41a,b** are identical with **41e** and **14g** in the previous paper (ref. 4).

28. At 0.1M Bu_3SnH, the ratio **40a/41a/42a** was 1/2.0/4.0. The isolated yield of **42a** was 58%.

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