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# Atom Transfer Addition and Annulation Reactions of Propargyl Iodomalononitrile

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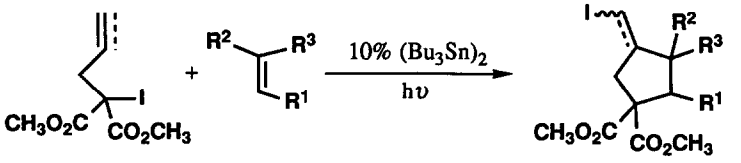
***Summary:*** *Heating of propargyl iodomalononitrile with mono-, di- or trisubstituted alkenes followed by reduction of the crude or isolated products with tributyltin hydride produces dicyano(methylene)cyclopentanes in good to excellent overall yield. This radical annulation is often highly regio and stereoselective. The mechanism is discussed.*

**Introduction:** The construction of five-membered carbocyclic rings[2] from alkenes is one of the most important general tactics in organic synthesis. Multi-step transformations are common, so one-step or "one-pot" transformations—termed annulations[3]—are especially valued. Virtually all such methods require the participation of activated alkenes, and activation is typically accomplished by attachment of either strong electron withdrawing groups (carbonyl, sulfonyl, etc.) or electron donating heteroatoms. General annulative methods that use unactivated alkenes as components would be very useful given the ready availability of these alkenes. We have targeted this goal by developing the chemistry of electrophilic radicals, which are among the few reactive intermediates that will reliably react with unactivated alkenes to form carbon-carbon bonds under mild conditions. In a detailed study, we demonstrated that propargyl (and allyl) iodomalonic esters were excellent reagents for annulations of methylene- (and methyl)-substituted cyclopentane rings to terminal and 1,1-disubstituted alkenes (eq 1).[4] Unfortunately, annulations with 1,2-disubstituted alkenes (both cyclic and acyclic) gave very poor yields, presumably because the initial radical addition step was not sufficiently rapid. The failure of cyclic alkenes to participate is disappointing (if not surprising) because the construction of fused rings by the annulation of new rings to preexisting ones will not be possible.



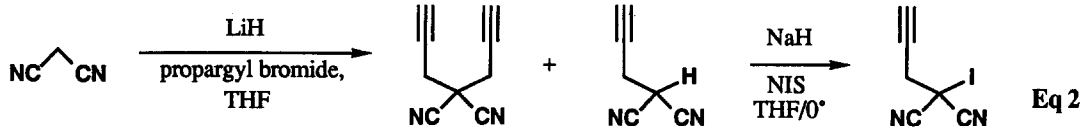

Eq 1

$R^2$, $R^3$ = alkyl, phenyl, good yield if $R^1$ = H
poor yield if $R^1 \neq H$

In an attempt to extend the generality of atom transfer annulation reactions of electrophilic radicals, we turned next to the chemistry of malononitrile radicals. Detailed studies by Boldt showed that the parent malononitrile radical has a much better reactivity profile than its malonic ester counterpart,[5] and it adds in good yields to a variety of di- and trisubstituted alkenes. As far as we are aware, there are no examples of halogen transfer addition reactions of substituted malononitriles;[6] however, it is likely that alkyl-substituted malononitrile radicals will add *more slowly* to alkenes than the parent.[7] We now report the full details of our preparative studies on atom transfer annulation reactions of propargyl iodomalononitrile.[8] Some mechanistic observations are also included, and the mechanism is discussed We describe parallel studies on

the annulation reactions of allyl iodomalononitriles in the following paper.[9] Taken together, these results indicate that iodomalononitriles are an important new class of reagents that significantly extend the preparative scope with reactions of electrophilic radicals. These reagents will be useful for atom transfer addition and annulation reactions with many classes of unactivated alkenes. Finally, the products of the annulation reactions, dicyanocyclopentanes, offer unique opportunities for subsequent transformations.

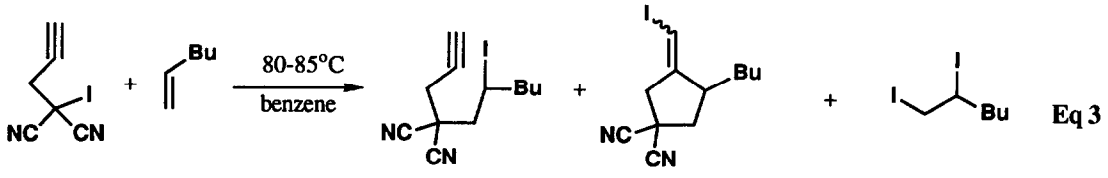
**Preparative Experiments:** Eq 2 outlines the synthesis of propargyl iodomalononitrile (**1**), the reagent used in all the experiments described in this paper.[10] Selective monopropargylation of malononitrile (**2**) was not an easy task. Under most conditions, dipropargyl derivative **3** was the major product, alongside the desired product **4** and recovered **2**. After extensive variation of conditions, we finally produced an acceptable yield of **4** (43% isolated) by generation of the lithium salt of **2** in THF, followed by slow addition of propargyl bromide. Initial attempts to iodinate **4** by using our standard conditions for the synthesis of iodomalonic esters were not encouraging. Deprotonation of **4** with NaH (THF, 0°C) resulted in a yellow solution that turned dark purple within 30 min. We isolated no iodide **1** upon quenching of either the yellow or dark solution with *N*-iodosuccinimide (NIS) or $I_2$. After several trials, we fortunately discovered that simple admixing of all the reagents together solved the problem. Thus, addition of a THF solution of **4** to a mixture of NIS, NaH, and THF, followed by stirring for 1 h at 0°C and flash chromatography, formed **1** in 93% yield.[11] This reaction must be conducted in the dark, and longer reaction times resulted in extensive decomposition of **1**. Iodomalononitrile **1** was stable for about 3 weeks at –20°C in the dark, but it was generally prepared and used directly.




Eq 2

**2** **3** **4** **1**

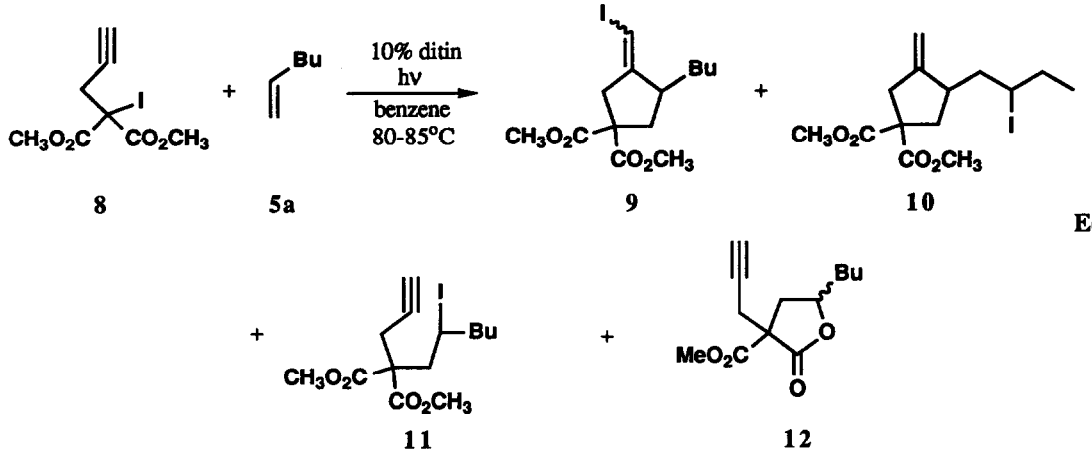
We were surprised by the results of the first annulation experiments with **1**. Sunlamp irradiation of **1** and 1-hexene (**5a**, 2 equiv) in the presence of 10% hexabutylditin produced only trace amounts (<5%) of the annulation product **7a** along with the product of atom transfer addition, **6a**. From this rather complex reaction mixture, we isolated **6a** in 42% by chromatography. This reaction differs significantly from that of the iodomalonate **8** (eq 4).[4a] Reaction of **8** and **5a** under the same reaction conditions produced annulation products **9** and **10** (compound **10** results from 1,5-hydrogen transfer prior to iodine transfer). Atom transfer addition product **11** was observed in small amounts at early reaction times reaction, but it was consumed at the end. The reaction of **8** was considerably cleaner than that of **1**, and the isolated yield was higher (62%). The reaction mixture with **8** remained clear throughout most of the irradiation, whereas that with **1** rapidly turned dark.




Eq 3

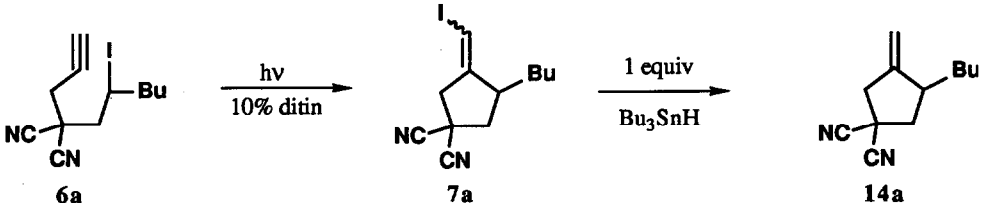
**1** **5a** **6a** **7a(E & Z)** **13**

| | | |
|---|---|---|
| hν/ditin | 42% | <5% |
| hν | 88% | <5% |
| heat | 95% | <5% |




Eq 4

Control experiments quickly identified a key problem: iodomalononitrile **1** and hexabutylditin react rapidly with each other under the reaction conditions.[12] We next repeated the initial experiment without adding ditin. Simple photolysis of **1** and **5a** for 45 min produced **6a** and **7a** (E/Z) in a ratio of >20/1. We now isolated adduct **6a** in 88% yield. 1,2-Diiodohexane (**13**) was also formed in significant amounts (~5%) in this reaction, although we did not attempt to isolate it. We prepared an authentic sample of **13** by refluxing $I_2$ and 1-hexene in benzene. Since the tint of molecular iodine is clearly visible at the start of the photolysis and darkens significantly during the reaction, we suspect that **13** originates by reversible addition of $I_2$ to **5a**.[13] Sunlamp irradiation of pure **6a** in the presence of 10% hexabutylditin (eq 5)[14] now induced a smooth isomerization to **7a** (78% yield, 2.6/1, E/Z). Reduction of either **6a** or **7a** with 1 equiv of tributyltin hydride (eq 5) produced **14a** as the only product (88% isolated yield from **7a**).

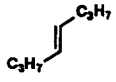
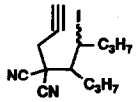
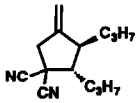
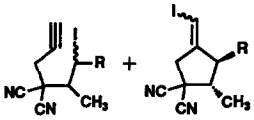
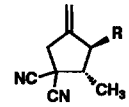
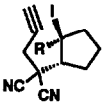
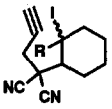
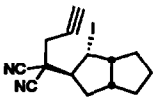
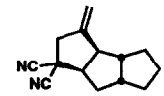
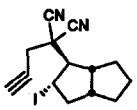
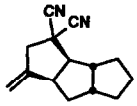



Eq 5

For the purposes of comparison, we repeated the annulation reaction of **8** and **5a** in the absence of ditin. From this reaction, we isolated vinyl iodides **9E/Z** (11%), atom transfer addition product **11** (42%), and epimeric lactones **12** (18%). Lactones **12** result from simple ionic lactonization of **11**.[4a] We believe that the striking differences in product distributions in the reaction of **8** are due to molecular iodine, which is rapidly trapped by ditin, but builds to significant concentration when ditin is absent. This is discussed in the section on mechanism.

We then began to investigate the generality of this procedure, focusing on 1,2-di- and trisubstituted alkenes. (It seems certain that mono- and 1,1-disubstituted alkenes should react in excellent yields.) The results are summarized in Table 1 under the column headed "hv". By conducting a few comparison experiments, we soon discovered that irradiation was neither necessary nor even beneficial. Although significantly longer reaction times were required, we obtained the best yields of adducts **6** simply by heating **1** and **5** (2 equiv) at reflux in benzene in the dark. This method was adopted as the standard procedure, and the results of a series of experiments are summarized in Table 1 under the column headed "Heat".

**Table 1. Atom Transfer Addition and Annulation Reactions of 1**

| Entry | Alkene | Product(s) | hν[a] | Heat[b] | Time | Reduction | Yield |
|---|---|---|---|---|---|---|---|
| a | **5a**[c] | **6a**[c] | 88% | 95% | 5 h | **14a**[c] | 86% |
| |  |  | | | |  | |
| b | **5b** | **6b** | 28% (1/1)[d] | 62% (1.1/1)[d] | 10 h | **14b** | 59% |
| |  |  | | | |  | |
| c | **5c** R = Ph (trans) | **6c** + **7c** | — | 98%[e] | 72 h | **14c** | 82% |
| d | **5d** R = *i*-Pr (cis) | **6d** + **7d** | — | 82%[f] | 72 h | **14d** | 76% |
| |  |  | | | |  | |
| e | **5e** R = H | **6e** | 70% | 88%[g] | 5 h | **14e** | 83% |
| f | **5f** R = $CH_3$ | **6f** | 76% | (95%)[g,h] | 24 h | **14f** | 63%[j] |
| |  |  | | | |  | |
| g | **5g** R = H | **6g** | 37% (1.8/1) | 74% (2/1)[i] | 12 h | **14g** | 79% |
| h | **5h** R = $CH_3$ | **6h** | — | 72%[h] | 24 h | **14h** | 45%[j] |
| | |  | | | |  | |
| i |  | +  | — | 90% (1.5/1) | 7 h | +  | 81% (1.5/1.0) |
| | **5i** | **6i** + **6j** | | | | **14i** + **14j** | |

**Footnotes to the Table**

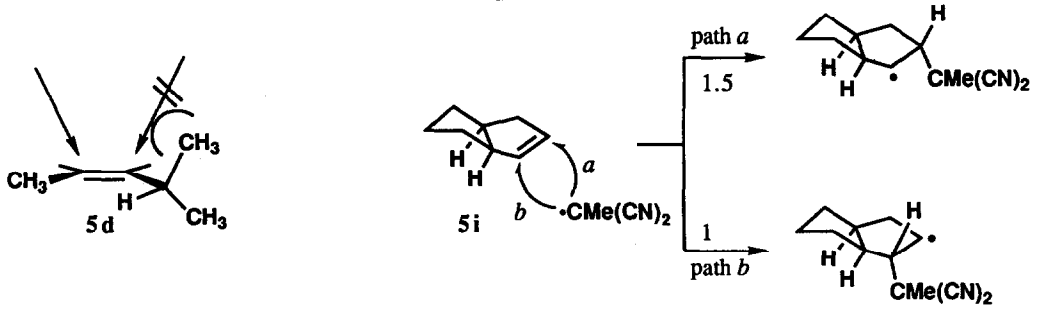
a) Sunlamp irradiation of an 0.3M benzene solution of **1** and **5** for 30-60 min. b) Heating of an 0.3M benzene solution of **1** and **5** at 80°C in the dark for the indicated time. c) See eq 3 for structures. d) Mixture of diastereomers, stereochemistry not assigned. e) After 72 h, only vinyl iodides **7cE/Z** (2.4/1) were present. f) The final ratio **6d-major/6d-minor /7dE/7dZ** was 3.0/1.0/2.3/1.5). g) Only the trans isomer was detected. h) Yield of crude product after filtration through $SiO_2$. i) trans/cis. j) Crude iodide was used; overall yield from **1**.

Good to excellent yields of adducts were obtained by this very simple procedure with di- and trisubstituted alkenes. Currently, there are no other classes of carbon-centered radicals that will add to the alkenes in Table 1 in such good yields. For example, the reaction of iodomalonic ester 8 with cyclohexene (**5g**) did not produce significant quantities of atom transfer addition or annulation products. In contrast, reaction of **1** and **5g** produced **6g** in 74% isolated yield (entry g). Indeed, there are only a few reactive intermediates of any sort that will directly form carbon-carbon bonds with the alkenes in Table 1.

Reaction times varied from 5 h to 72 h as a function of alkene substitution pattern.[15] In most cases, atom transfer adducts **6** were the major products in the reactions, but at least traces (1-5%) of annulation products were usually formed. 3°-Iodides were stable to chromatography, and Table 1 records isolated yields; however, some of these iodides were not stable to storage and they were often only partially characterized. We fully characterized the cyclic products (**14**) derived from **6**. The 3°-iodides (entries f and h) were not stable to isolation (although we did obtain good $^1$H NMR spectra of the crude products), and they were directly converted to the cyclic products. Two alkenes gave significant amounts of (iodomethylene)-cyclopentanes during the heating. With *cis*-4-methyl-2-pentene (entry d), adduct **6d** and (iodomethylene)-cyclopentane **7d** both formed from the beginning of the reaction, and their ratio changed relatively little over time. We conclude that **7d** is a direct reaction product, and that it is not formed through the intermediacy of **6d**. In contrast, the reaction with β–methyl styrene (entry c) produced only adduct **6c** at very short reaction time, and the ratio **6c/7c** steadily decreased during the reaction. After 3 d, **6c** was consumed and **7c** was the only product. Clearly benzylic iodide **6c** is isomerizing to **7c** during the reaction.

With one exception (entry i), each of the unsymmetrical alkenes gave a single regioisomeric product. Mono- (entry a) and trisubstituted (entries f, h) alkenes gave products resulting from addition to the less-substituted end of the alkene. β-Methyl styrene gave addition β to the phenyl group (entry c). These observations are in line with expected behavior for radicals. *cis*-4-Methyl-2-pentene gave addition β to the isopropyl group (entry d). In contrast, bicyclooctene **5i** (entry i), which has the same substituent and branching pattern as **5d**, exhibited very low regioselectivity.[16] These observations are rationalized in Figure 1. In the lowest energy rotamer of **5d**, A-strain dictates that the methyl groups shield both faces of the carbon adjacent to the isopropyl group.[17] This is not true for the cyclic alkene **5i**. The selectivity with **5i** is still notable since only two (**6i**, **6j**) of eight possible isomers are observed.

**Figure 1**




Stereoselectivity in the formation of **6** is generally low for acyclic alkenes (entries b, d) and cyclohexenes (entries g, h), but there is a high trans selectivity for cyclopentenes (entries e, f, i). In most cases, the stereoisomer ratios change little during the reaction, so we believe that those reported in Table 1 are at least close to the kinetic ratios. The stereoselection arises in the iodine transfer step, and it is already known that cyclopentyl radicals typically give higher levels of stereoselection than cyclohexyl radicals.[18] There is one dramatic exception to these generalizations: β-methyl styrene (**5c**) gives initial levels of stereoselection that are very high, but that change during the course of the reaction.[19] Follow-up experiments showed that additions of iodomalononitriles to pairs of E/Z alkenes are not stereospecific.[20]

This is strong evidence for a radical mechanism because ionic additions of iodonium ions should be stereospecific. However, benzylic radicals do abstract iodine stereoselectively, and this accounts for the high levels of selectivity in formation of **6c** at early reaction times.[20] Our data[19] also indicate that benzylic iodides **6c** donate iodine with selectivity (**6c-syn** is a better iodine donor than **6c-anti**).

All of the adducts **6** (either crude or purified) cyclized in excellent yields upon standard reduction with tributyltin hydride (0.3M, 80°C), as shown in Table 1 under the heading "Reduction". Many of the iodides **5** were isolated and purified prior to reduction. However, this procedure seems to offer no advantage over simple reduction of the crude product, which gave **7** in comparable (sometimes better) yields. In all cases, we observed only products of 5-exo cyclization. There were no products of 6-endo cyclization, nor were reduced, uncyclized products formed (despite the relatively high initial tin hydride concentration of 0.3M). These observations can be attributed largely to the geminal dicyano group, which significantly accelerates the radical cyclization (the so-called "gem-dimethyl effect").[21] In each cyclization, only a single stereoisomer formed. Bicyclic systems formed with a cis fusion, as expected (entries e-i). In contrast, simple cyclopentenes formed as single stereoisomers (entries b-d) that were ultimately assigned as trans by analogy to **7cZ**, whose structure was determined by an x-ray crystal diffraction study.[22] A plot of this structure is shown in Figure 2. These are among the first observations of stereoselectivity for this particular class of radical cyclizations.[23] Figure 3 shows that the high trans selectivity is nicely rationalized by applying Beckwith's guidelines.[24]

**Figure 2. Crystal Structure of 7cZ.**

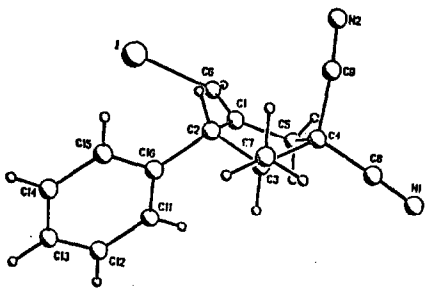
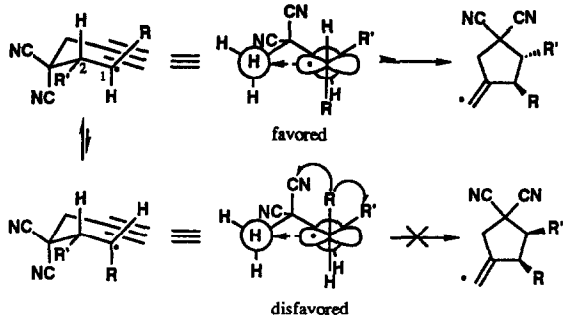
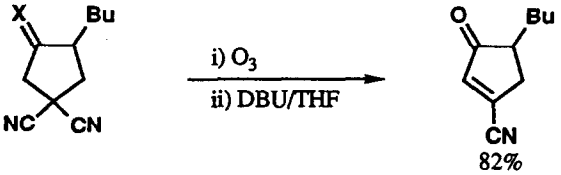


**Figure 3**




**Transformations of Products:** Given that the geminal dinitrile is a relatively uncommon functionality in synthesis, we felt that it was imperative to develop methods to convert our annulation products to more common functionalities. We have already reported a tin hydride reduction of related geminal dinitriles to mono-nitriles under mild conditions,[25] and this transformation would clearly be applicable to the products in Table 1. As eq 6 illustrates, the annulation products are also readily converted to β-cyano cyclopentenones. Ozonolysis of **14a**, followed by direct treatment of the crude β,β-dicyanoketone **15** with DBU, provided β-cyanoenone **16** in 82% overall yield.

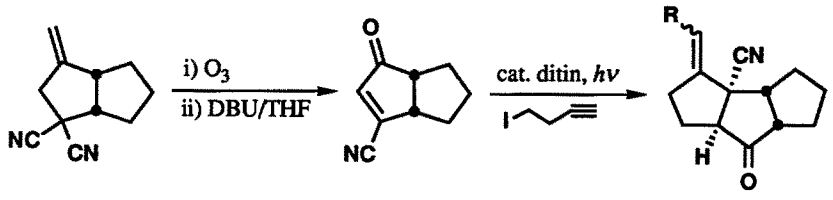



82%

**14a** X = $CH_2$
**15** X = O
**16**

Eq 6

Such β-cyanoenones should be especially useful for subsequent modification by standard ionic or pericyclic reactions. Eq 7 illustrates that they will also be excellent radicophiles for nucleophilic radicals. Ozonolysis of **14e** and subsequent DBU treatment provided **17** in 87% yield. Next, an atom transfer annulation reaction of iodobutyne and **17** under our standard conditions[26] provided **18E/Z** in 81% isolated yield.[27] This yield is significantly higher than those that we observed in related annulations, probably reflecting the high reactivity of **17** as a radical acceptor. In a separate experiment, atom transfer annulation, followed by direct reductive deiodination with tributyltin hydride, provided **19** in 75% yield from **17**. Overall, functionalized triquinane **19** is available in three operations from cyclopentene in 57% yield. This illustrates how complex molecules can rapidly be assembled by combining nucleophilic and electrophilic radical annulation chemistry.




Eq 7

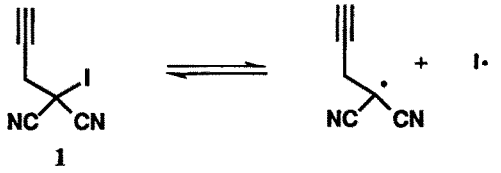
**14e** **17**, 87% **18** (E & Z) R = I, 81%
**19** R = H, 75%

**Mechanistic Experiments and Discussion:** We recently provided good evidence that iodomalonic esters react via standard radical chains.[4] However, because propargyl iodomalononitrile behaves differently from the (apparently) closely related iodomalonic esters, it is not at all obvious that direct mechanistic analogies can be drawn. The differences that must be rationalized in any mechanistic analysis are summarized as follows: 1) iodomalononitriles add to representative di- and tri-substituted alkenes in good yields while iodomalonic esters do not; 2) the use of 10% ditin improved both the reaction rate and yield for iodomalonic esters, but it was actually detrimental in the reactions of iodomalononitriles, 3) sunlamp irradiation of iodomalonic esters increased both the rate and the yield of products while sunlamp irradiation of iodomalononitriles increased the rate but decreased the yield (relative to simple heating in the dark); 4) reactions with propargyl iodomalononitrile normally stopped at the adduct stage (although small amounts of annulation products were usually present) while reactions of propargyl iodomalonic esters usually proceeded directly to the annulated products (although small amounts of adducts were sometimes detected).

At first, we suspected that the reactions of iodomalononitriles might occur through the intermediacy of iodonium ions, not radicals. We have already observed ionic reactions of related iodoacetoacetates.[28] However, several lines of evidence now suggest that radical intermediates are involved. First, we could not promote the reaction with additives that might have been expected to facilitate iodonium ion formation: addition of molecular iodine had little effect on the rate or yield in the reaction of **1** with **5**, while tetrabutylammonium iodide rapidly deiodinated **1** to give back **4**. Second, addition of the radical scavenger TEMPO to reactions involving **1** completely suppressed formation of the products, but resulted in complex reactions mixtures from which no major products were identifiable. Third, the regiochemistry with β-methyl styrene (entry c) is consistent with a radical addition β- to the phenyl group. Nucleophiles should add α to the phenyl group in iodonium ions derived from β-methyl styrene. Fourth, and most compelling, the addition reactions are not stereospecific.[20] Therefore, we now believe that radical intermediates are involved in all these reactions of iodomalononitriles.

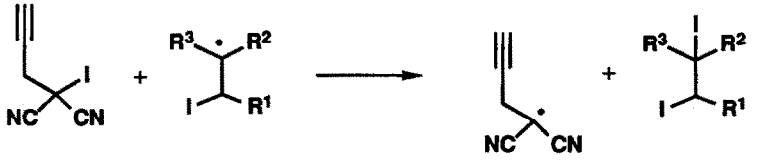
Eqs 8-17 outline the reasonable possibilities for steps in a radical mechanism, and we consider both chain and non-chain mechanisms. A standard atom transfer chain is readily formulated. Initiation might either involve direct homolytic cleavage of the C–I bond (as eq 8 shows), or molecule induced homolysis

(as eqs 9 and 10 show). Boldt has proposed the molecule induced homolysis as an initiation step in his reactions of bromomalononitriles to account for the formation of 1,2-dibromides.[5] We also observed 1,2-diiodides in some reactions. However, when ditin is absent, molecular iodine is clearly present, so we believe that the diiodide formed in our reactions can be accounted for by the reversible addition of $I_2$ to the alkene (eq 11). Whether or not the diiodide is observed then depends on the concentration of $I_2$ that builds during the reaction and the equilibrium constant for addition.[12]




Eq 8


Eq 9

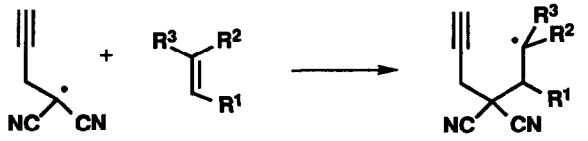



Eq 10

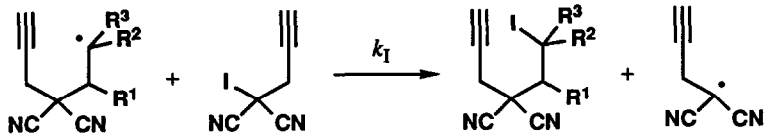

Eq 11

Propagation steps in a standard chain reaction include radical addition (eq 12), and atom transfer prior to cyclization (eq 13), or after cyclization (eq 14). Given that molecular iodine is clearly present and that it donates iodine atoms to most radicals at rates approaching the diffusion controlled limit,[29] we must also consider eq 15 as viable. Iodine transfer from $I_2$ forms the product, but does not propagate a chain. The combination of either radical generation process (eq 8 or eq 9 + 10) with radical addition (eq 12, with or without cyclization) and iodine transfer from $I_2$ (eq 15) defines a non-chain mechanism when the recombination shown in eq 16 is included.

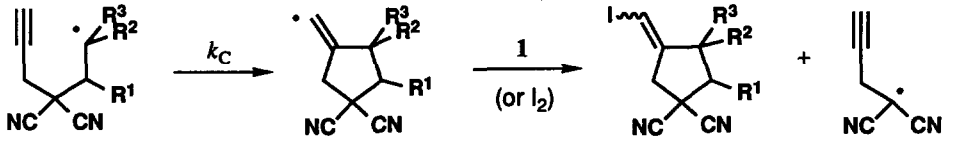
Finally, we must consider the reaction in eq 17 as another possible means of radical generation. This abstraction of an iodine atom by I• is endothermic, and normally it should much too slow to be important.[30] Indeed, the reverse of this reaction (which is usually thought to be diffusion controlled) is the cause of suppression of chains by $I_2$. However, we can estimate[31] that the C–I bond dissociation energy of an iodomalononitrile could be sufficiently low that the forward rate constant for eq 17 could be as high as $10^4$-$10^6$ $M^{-1}$ $s^{-1}$. We can then formulate an unusual chain by combining this radical generation step (eq 17) with addition (eq 12) and abstraction from iodine (eq 15). In this chain, molecular iodine (normally a powerful chain suppressant) is a catalyst!



Eq 12

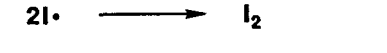


Eq 13



Eq 14

Eq 15



Eq 16

Eq 17

We now use these steps as a framework to discuss the observations with the propargyl iodomalononitrile and the differences between iodomalononitriles and iodomalonic esters. The differences in yield as a function of alkene substitution may be due either to the smaller size or the higher electrophilicity of the malononitrile radical relative to the malonic ester radical (or both).[32] Iodomalononitrile **1** is itself a terminal alkyne, so it is noteworthy that good yields of adducts with di- and trisubstituted alkenes can be obtained in the presence of this alkyne. We speculate that the inductive effect of the two nitriles deactivates **1** with respect to attack by an electrophilic malononitrile radical.

We believe that ditin improves the reaction rate and yield with malonic esters because it is an effective trap of $I_2$.[26] Molecular iodine presumably suppresses chain reactions by donating iodine atoms to all carbon-centered radicals, thereby breaking chains. Ditin does not improve the reactions of iodomalononitriles simply because the iodomalononitriles react with ditin. Thus, the more ditin that is added, the lower the yield of adducts in the reaction of **1** with 1-hexene. Adducts that do form simply result from reactions of residual **1** that survived the ditin treatment. When 1 equiv of ditin is added, all of **1** is destroyed and no adduct is formed. Thus, all the malononitrile reactions that we have conducted have $I_2$ present, and we do not currently know how these reactions would behave in the absence of $I_2$. This lack of knowledge clouds the mechanistic picture, but we can still suggest some reasonable possibilities that summarize our

current state of understanding.

Why does the product distribution change (eq 4) when propargyl iodomalonic ester **8** and 1-hexene are irradiated in the presence of ditin ($I_2$ absent) or its absence ($I_2$ present)? There are two possibilities. First, $I_2$ is a better iodine donor than **8** and it can trap adduct radicals prior to cyclization if its concentration is sufficiently high. This could explain the increased amount of **11** and **12** (which is derived from **11**) in the reaction without ditin. A second explanation is that the $I_2$ simply inhibits the chain isomerization of **11** to **9**. We have previously observed that hexynyl iodides will not isomerize to vinyl iodides unless $I_2$ is excluded.[26] The absence of **10** in the reaction without ditin suggests that a more efficient radical trap is present in this reaction (iodine transfer is faster than 1,5-hydrogen transfer), and this suggests that molecular iodine must play some role as an iodine donor. If **8** were the sole donor, then the ratio of **9/10** should be unchanged in these two experiments.

Why are atom transfer reactions of alkyl iodides completely suppressed by molecular iodine while those of iodomalonates are only retarded and those of iodomalononitriles proceed well? This must be related to the ability of these iodides to form radicals and to the ability of the derived radicals to react further with acceptors in the presence of $I_2$. Chain initiation from alkyl iodides is relatively inefficient (compared to iodomalonic esters and iodomalononitriles). Further, once the alkyl radicals are generated, they will react with $I_2$ at diffusion controlled rates. Thus, the chain reactions of alkyl iodides are easily inhibited. The C–I bonds in iodomalonic esters are weaker than those in alkyl iodides so initiation should be more efficient. Further, due to the weak C–I bond, the "back reaction" of a malonic ester radical with $I_2$ may no longer be diffusion controlled. Thus, the radicals will have more lifetime to react with acceptors. Iodomalononitriles take these considerations one step further. Clearly the initiation reactions of iodomalononitriles are very efficient. Indeed, we believe that photolysis gives poorer yields than heating in the dark is because photolytic initiation is too efficient. If initiation (eq 8 or eq 9 + 10) becomes fast relative to radical addition (eq 12), then radical concentrations build and yields will be decreased by radical–radical reactions. Further, the C–I bond of an iodomalononitrile is probably weaker than that of an iodomalonic ester,[33] and the back reaction of this radical with $I_2$ may not be diffusion controlled. Coupling this slower back reaction with the higher reactivity of the malononitrile radical towards acceptors results in severe erosion of the ability of $I_2$ to inhibit the chains. So much so that we must raise the following question:

Do the reactions of iodomalononitriles proceed by a chain or a non-chain mechanism? This is not an easy question to answer. That the reactions proceed so well in the presence of $I_2$ suggest that a non-chain mechanism is viable. However, that $I_2$ may not be a very efficient chain suppressor (see above) for malononitrile radicals supports the conclusion that chains may still be able to propagate. The key stage in determining a chain or non-chain mechanism is the partitioning of radicals between iodine abstraction from **1** (eq 13) and $I_2$ (eq 15). Transfer of iodine from $I_2$ (eq 15) probably occurs at rates approaching the diffusion controlled limit; however, iodomalononitrile **1** could well be every bit as good an iodine atom donor as $I_2$.[34] Throughout most of the reaction, the concentration of **1** must exceed the concentration of $I_2$, so we conclude that propagation of atom transfer chains under these conditions is possible. However, we know neither the chain length nor the relative contribution of the non-chain mechanism in product formation.

**Conclusions:** Propargyl iodomalononitrile **1** is the first member of a new class of annulation reagents. This reagent reacts with unactivated di-and trisubstituted alkenes. After tin hydride treatment, useful products are formed with high levels of regio- and stereoselectivity. The atom transfer reactions of **1** are significantly different from that of typical iodomalonic esters, yet these reactions still occur by a radical mechanism. However, we do not yet understand the role of molecular iodine (if any) in the reactions of iodomalononitriles. Our results suggest that substituted iodomalononitriles will be an interesting class of reagents for radical annulation reactions, and they also indicate the simple atom transfer addition reactions of these reagents should have broad generality. Reactions of allyl iodomalononitriles are described in the following paper.[9]

## Experimental

**General:** All reactions were performed under a nitrogen atmosphere. Iodides were handled in the dark, and reactions with these compounds were run in flasks covered with aluminum foil. Benzene, diethyl ether, and tetrahydrofuran were dried from sodium/benzophenone by distillation under an inert atmosphere. *N,N*-Dimethylformamide (DMF), 1,2-dichloroethane and triethylamine were distilled from calcium hydride. The reaction products are listed in order of increasing polarity. Nuclear magnetic resonance spectra were recorded at 300 MHz for $^1$H and 75 MHz for $^{13}$C. Analytical gas chromatography (GC) was performed on an HP-5890 instrument equipped with a fused silica capillary column (SPB-1, 30 M, 0.25 μm, 0.32 mm ID) and a flame ionization detector (FID) with helium as a carrier gas. GC-MS spectra were obtained on an HP-5890 instrument and an HP-5970 mass selective detector.

**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 yellow oil.

**General Procedure for Atom Transfer Additions of α-Iodomalononitriles.**

Iodomalononitrile **1** (1 equiv, 0.15-0.3 M) and an alkene (1-2 equiv) were heated in the dark in degassed benzene for 5-72 h at 80 °C under $N_2$. The progress of the reaction was monitored by TLC or NMR. After the iodomalononitrile was consumed, the mixture was concentrated under reduced pressure, and the crude product was purified by flash column chromatography to afford the corresponding iodide.

**2-Iodo-2-cyanopent-4-ynenitrile (1),** (93% yield, 10% EtOAc in hexanes).
$^1$H NMR ($CDCl_3$) δ 3.32 (2H, d, J = 2.7 Hz), 2.62 (1H, t, J = 2.7 Hz); $^{13}$C NMR ($CDCl_3$) δ 113.43 (s), 76.34 (d), 75.79 (s), 35.12 (t), 25.54 (s); IR (thin film) 3310, 2960, 2930, 2870, 2550, 2140, 1440, 1250, 1090, 800, 680 cm$^{-1}$; MS (*m/e*) 230 ($M^+$), 228, 103 ($M^+ - I$), 76, 47.

**2-Cyanopent-4-ynenitrile (4); 2-Cyano-2-(1-propynyl)pent-4-ynenitrile (3).**

The anion of malononitrile was prepared by treatment of **2** (2.00 g, 30.27 mmol) with LiH (0.12g, 15.14 mmol) in THF (50 mL) at 0 °C. After 15 min, propargyl bromide (1.80 g, 15.14 mmol) in THF (50 mL) was slowly added. The reaction mixture was stirred for 3 h at 25 °C, and then poured into cold water. After extractive workup, purification of the residue (silica gel, 15% EtOAc in hexanes) afforded **4** (0.68g, 43%) and **3** in a ratio of 1.6:1.0 as slightly yellow liquids: **4** $^1$H NMR ($CDCl_3$) δ 3.96 (1H, t, J = 6.6 Hz), 2.93 (2H, dd, J = 6.6, 2.6 Hz), 2.39 (1H, t, J = 2.6 Hz); $^{13}$C NMR ($CDCl_3$) δ 111.57 (s), 75.11 (s), 74.79 (d), 22.94 (d), 21.70 (t); IR (thin film) 3300, 2980, 2930, 2850, 2265, 2130, 1430, 1040, 810 cm$^{-1}$; **3** $^1$H NMR ($CDCl_3$) δ 3.07 (4H, d, J = 2.7 Hz), 2.42 (2H, t, J = 2.7 Hz); $^{13}$C NMR ($CDCl_3$) δ 113.49 (s), 75.82 (d), 73.94 (s), 35.97 (s), 27.33 (t); IR (thin film) 3300, 2970, 2930, 2270, 2140, 1430, 1090 cm$^{-1}$.

**4,4-Dicyano-6-iodo-1-decyne (6a).**

Compound **6a** was prepared by heating **1** (100 mg, 0.43 mmol) and 1-hexene (108 μL, 0.89 mmol) in benzene (1.45 mL) for 5 h. After chromatography (silica gel, 5% EtOAc in hexanes) **6a** was isolated in a yield of 95% (130 mg) as a slightly yellow liquid: $^1$H NMR ($CDCl_3$) δ 4.29 (1H, m), 2.99 (2H, d, J = 2.5 Hz), 2.77 (1H, dd, J = 6.9, 14.9 Hz), 2.66 (1H, dd, J = 7.2, 14.9 Hz), 2.43 (1H, t, J = 2.5 Hz), 1.88 (2H, m), 1.58 (1H, m), 1.50-1.28 (3H, m), 0.94 (3H, t, J = 6.7 Hz);$^{13}$C NMR ($CDCl_3$) δ 114.22 (s), 113.61 (s), 76.02 (d), 74.14 (s), 45.74 (t), 39.37 (t), 36.51 (s), 31.56 (t), 29.65 (t), 25.95 (d), 21.65 (t), 13.92 (q); LRMS (*m/e*) 314 ($M^+$), 257, 231, 217, 199, 187, 160, 147, 133, 118, 105, 91, 67; HRMS calcd for $C_{12}H_{15}N_2I$, 314.0280, found, 314.0280.

**4,4-Dicyano-6-iodo-5-propyl-non-1-yne (6b).**

Compound **6b** was prepared heating **1** (100 mg, 0.43 mmol) and *trans*-4-octene (136 μL, 0.86 mmol) in

benzene (2.86 mL) for 10 h. Chromatography (silica gel, 10% EtOAc in hexanes) gave diastereoisomeric iodides **6b-major** and **6b-minor** (91 mg, in 62% combined yield) in a 1.2:1.0 ratio as yellow oils: (**major**) $^1$H NMR ($CDCl_3$) δ 4.59 (1H, dt, J = 11.6, 2.7 Hz), 3.04 (1H, dd, J = 2.7, 17.0 Hz), 2.94 (1H, dd, J = 17.0 Hz), 2.58 (1H, dt, J = 5.1, 2.7 Hz), 2.45 (1H, t, J = 2.7 Hz), 2.04 (2H, m), 1.66 (4H, m), 1.36 (2H, m), 1.03 (3H, t, J = 6.7 Hz), 0.96 (3H, t, J = 6.9 Hz); (**minor**) $^1$H NMR ($CDCl_3$) δ 4.40 (1H, dt, J = 2.7, 6.8 Hz), 3.12 (1H, dd, J = 2.7, 17.0 Hz), 3.00 (1H, dd, J = 2.7, 17.0 Hz), 2.41 (1H, dt, J = 2.7 Hz), 2.03 (1H, m), 1.82 (1H, m), 1.76-1.58 (6H, m), 1.43 (1H, m), 1.03 (3H, t, J = 6.7 Hz), 0.96 (3H, t, J = 6.9 Hz).

***trans*-1-(Propargyldicyanomethyl)-2-iodocyclopentane (6e).**

Compound **6e** was prepared by heating **1** (100 mg, 0.43 mmol) and cyclopentene (76 μL, 0.89 mmol) in benzene (1.45 mL) for 5 h. After chromatography (silica gel, 5% EtOAc in hexanes), **6e** was isolated in a yield of 88% (110 mg) as a yellow liquid: $^1$H NMR ($CDCl_3$) δ 4.24 (1H, ddd, J = 7.1, 4.6, 4.8 Hz), 3.11 (1H, ddd, J = 8.4, 8.4, 4.8 Hz), 3.02 (2H, d, J = 2.7 Hz), 2.44 (1H, t, J = 2.7 Hz), 2.41-2.12 (3H, m), 2.04-1.82 (2H, m) 1.71 (1H, m); $^{13}$C NMR ($CDCl_3$) δ 113.77 (s), 113.49 (s), 75.65 (d), 74.50 (s), 55.54 (d), 41.69 (s), 41.41 (t), 30.33 (t), 27.65 (t), 25.07 (d), 20.70 (t); LRMS (*m/e*) 298 ($M^+$), 171, 156, 144, 131, 116, 105, 93, 77, 67; HRMS calcd for $C_{11}H_{11}N_2I$, 297.9968, found, 297.9967.

***cis*-1,1-Dicyano-8-methyl-3-(methylene)bicyclo[3.3.0]octane(14f) via *trans*-Propargyl-(2-iodo-2-methylcyclopentyl)-malononitrile (6f).**

A solution of iodomalononitrile **1** (0.15g, 0.65 mmol) and 1-methylcyclopentene (137 μL, 1.30 mmol) in degassed benzene (4.4 mL) was heated for 24 h at 80 °C in the dark. The reaction mixture was diluted with ether (15 mL), filtered through silica gel, and concentrated to give the crude iodide **6f** (0.19 g, 95%): $^1$H NMR ($CDCl_3$) δ 3.27 (1H, t, J = 8.9 Hz), 3.10 (1H, dd, J = 16.7, 2.6 Hz), 2.93 (1H, dd, J = 16.7, 2.6 Hz), 2.58 (1H, m), 2.47 (1H, t, J = 2.7 Hz), 2.30 (3H, s), 2.06 (2H, m), 1.88 (2H, m), 1.78 (1H, m).

The subsequent reductive cyclization was conducted by addition of tributyltin hydride (175 μL, 0.65 mmol) and AIBN (11 mg, 0.07 mmol) to the solution of the crude iodide in benzene (2.2 mL). After refluxing for 3 h, the resulting mixture was diluted with ether (15 mL), treated with 1.2 equiv of DBU and $I_2$, and filtered through silica gel. Evaporation of solvent and purification by column chromatography (10% EtOAc in hexanes) gave **14f** (76 mg, 63%) as a clear oil: $^1$H NMR ($CDCl_3$) δ 5.13 (1H, t, J = 2.0 Hz), 5.06 (1H, t, J = 2.0 Hz), 3.08 (2H, t, J = 6.7 Hz), 2.67 (1H, t, J = 7.6 Hz), 2.18 (1H, m), 1.76-1.68 (5H, m), 1.34 (3H, s); $^{13}$C NMR ($CDCl_3$) δ 152.56 (s), 116.57, (s) 115.13 (s), 109.57 (t), 60.08 (d), 53.14 (s), 44.54 (t), 43.15 (t), 36.36 (s), 31.80 (t), 27.53 (q), 26.20 (t); IR (thin film) 3090, 2970, 2870, 2250, 1670, 1460, 910 $cm^{-1}$; LRMS (*m/e*) 186 ($M^+$), 171, 157, 144, 129, 108, 93, 79; HRMS calcd for $C_{12}H_{14}N_2$, 186.1154, found, 186.1157.

***trans*- & *cis*-1-(Propargyldicyanomethyl)-2-iodocyclohexane (6g).**

Compound **6g** was prepared by heating **1** (100 mg, 0.43 mmol) and cyclohexene (88 μL, 0.86 mmol) in benzene (1.45 mL) for 24 h. After chromatography (silica gel, 10% EtOAc in hexanes) **6g-trans** and **6g-cis** were isolated (99 mg, 74%) in a 2:1 ratio as yellow oils: **6g-trans** $^1$H NMR ($CDCl_3$) δ 4.36 (1H, dt, J = 3.8, 9.5 Hz), 3.34 (1H, dd, J = 2.6, 16.9 Hz), 3.12 (1H, dd, J = 2.6, 16.9 Hz), 2.54 (2H, m), 2.42 (1H, t, J = 2.6 Hz), 2.29 (1H, m), 2.15 (1H, m), 1.97 (1H, m), 1.62 (1H, m), 1.53 (3H, m); $^{13}$C NMR ($CDCl_3$) δ 114.48, 114.06, 75.71, 74.57, 47.52, 42.05, 39.98, 28.56, 28.44, 27.78, 26.56, 23.81; **6g-cis** $^1$H NMR ($CDCl_3$) δ 4.76 (1H, m), 3.10 (1H, dd, J = 2.6, 17.0 Hz), 2.98 (1H, dd, J = 2.6, 17.0 Hz), 2.42 (1H, t, J = 2.6 Hz), 2.27 (1H, m), 1.96 (1H, m), 1.84 (4H, m), 1.69 (1H, m), 1.53 (1H, m), 1.44 (1H, m).

***(E* and *Z)*-1,1-Dicyano-4-butyl-3-(iodomethylene)cyclopentane (7a).**

To a solution of **6a** (100 mg, 0.32 mmol) in benzene (1 mL) was added hexabutylditin (16 μL, 0.03 mmol). The mixture was irradiated with sunlamp at 80-85 °C for 3 h. An additional portion of hexabutylditin (8 μL) was added and irradiation was continued for 6 h. Concentration of the reaction mixture, followed by flash column chromatography (silica gel 5% EtOAc in hexanes), gave vinyl iodides **7a/E** and **7a/Z** (78 mg, 78% combined yield, in 2.6:1.0 ratio) as yellow liquids: **7a/E** $^1$H NMR ($CDCl_3$) δ 6.24 (1H, m), 3.27 (1H, broad d, J = 17.9 Hz), 2.97 (1H, dt, J = 17.9, 2.6

Hz), 2.92-2.74 (2H, m), 2.13 (2H, dd, J = 12.0, 1.5 Hz), 1.78 (2H, m), 1.60-1.22 (3H, m), 0.96 (3H, t, J = 7.1 Hz); **7a/Z** $^1$H NMR ($CDCl_3$) δ 6.38 (1H, m), 3.18 (1H, broad d, J = 15.1 Hz), 3.02 (1H, dt, J = 15.1, 1.9 Hz), 2.92-2.74 (2H, m), 2.29 (2H, m), 1.98 (2H, m), 1.60-1.22 (3H, m), 0.94 (3H, t, J = 7.1 Hz).

**(*E* and *Z*)-*trans*-1,1-Dicyano-5-methyl-4-phenyl-3-(iodomethylene)cyclopentanes (7c).**

Compounds **7c** were prepared by heating **1** (100 mg, 0.43 mmol) and *trans*-β-methylstyrene (58 μL, 0.43 mmol) in benzene (1.45 mL) for 72 h. After chromatography (silica gel, 5% EtOAc in hexanes) **7c/E** and **7c/Z** (E/Z = 2.4/1.0) were isolated in combined yield of 98% (149 mg) as white solids: **7c/E** mp 143-145 °C; $^1$H NMR ($CDCl_3$) δ 7.36 (3H, m), 7.16 (2H, m), 5.88 (1H, t, J = 2.6 Hz), 3.43 (1H, ddd, J = 2.0, 2.6, 18.0 Hz), 3.38 (1H, ddd, J = 2.0, 2.6,12.0 Hz), 3.00 (1H, ddd, J = 2.6, 2.8, 18.0 Hz), 2.67 (1H, broad dd, J = 6.6 Hz, 12.0 Hz), 1.25 (3H, d, J = 6.6 Hz); $^{13}$C NMR ($CDCl_3$) δ 149.69 (s), 137.34 (s), 129.22 (d), 128.63 (d), 128.42 (d), 114.99 (s), 113.94 (s), 78.18 (d), 57.23 (t), 52.63 (t), 48.06 (t), 38.39 (s), 13.54 (q); LRMS (*m/e*) 348 ($M^+$), 321, 306, 221, 182, 134, 107, 91, 77, 55; HRMS calcd for $C_{15}H_{13}N_2I$, 348.0120, found, 348.0120; **7c/Z** mp 153-155 °C; $^1$H NMR ($CDCl_3$) δ 7.34 (3H, m), 7.15 (2H, m), 6.63 (1H, t, J = 2.6 Hz), 3.48 (1H, dd, J = 15.2, 1.0 Hz), 3.30 (1H, dt, J = 10.5, 2.6 Hz), 3.24 (1H, broad t, J = 15.2 Hz), 2.58 (1H, dddd, J = 10.5, 6.6, 2.6, 1.0 Hz), 1.41 (3H, d, J = 6.6 Hz); $^{13}$C NMR ($CDCl_3$) δ 146.84 (s), 139.60 (s), 129.14 (d), 128.52 (d), 127.53 (d), 114.62 (s), 113.39 (s), 79.00 (d), 57.29 (t), 54.77 (t), 48.14 (t), 39.45 (s), 13.75 (q); MS (*m/e*) 348 ($M^+$); IR (thin film, E/Z mixture) 3090, 3050, 2980, 2940, 2860, 2250, 1460, 1120, 760, 710, 680 $cm^{-1}$.

**4,4-Dicyano-5,7-dimethyl-6-iodooct-1-yne (6d), and (*E* and *Z*)-*trans*-1,1-Dicyano-4-isopropyl-5-methyl-3-(iodomethylene)cyclopentanes (7d).**

Compounds **6d** and **7d** were prepared by heating **1** (100 mg, 0.43 mmol) and *cis*-4-methyl-2-pentene (109 μL, 0.86 mmol) in benzene (1.45 mL) for 72 h. Cyclic iodides **7d** (E/Z = 1.5:1.0) and acyclic iodides **6d** (major:minor = 3.0:1.0) were obtained by column chromatography (silica gel, 5% EtOAc in hexanes) in a combined yield of 82% (110 mg) as yellow oils. The ratio **6d:7d** was 4.0:3.8: **7d/E** $^1$H NMR ($CDCl_3$) δ 6.25 (1H, dt, J = 1.7, 3.0 Hz), 3.31 (1H, dd, J = 1.7, 16.5 Hz), 2.78 (1H, dt, J = 16.5, 2.6 Hz), 2.48 (1H, dd, J = 6.7, 9.9 Hz), 2.32 (1H, m), 1.39 (3H, d, J = 6.7 Hz), 0.98 (3H, d, J = 6.9), 0.96 (3H, d, J = 6.9); **7d/Z** $^1$H NMR ($CDCl_3$) δ 6.43 (1H, t, J = 2.1 Hz), 3.14 (1H, d, J = 14.3), 2.83 (1H, dt, J = 2.0, 15.5 Hz), 2.61 (1H, broad dd, J = 6.9, 7.7 Hz), 2.36 (1H, m), 1.45 (1H, d, J = 6.9 Hz), 1.02 (3H, d, J = 6.9 Hz), 0.85 (3H, d, J = 6.9 Hz); $^{13}$C NMR ($CDCl_3$, E/Z mixture) δ 148.52, 148.22, 115.29, 115.28, 113.91, 113.68, 76.57, 75.48, 55.47, 48.88, 47.88, 47.65, 44.90, 39.05, 39.04, 29.89, 29.02, 20.93, 19.36, 19.37, 18.15, 17.05, 16.43, 15.33; **6d-minor** $^1$H NMR ($CDCl_3$) δ 4.70 (1H, dd, J = 4.0, 2.7 Hz), 3.08 (1H, dd, J = 2.7, 17.0 Hz), 2.94 (1H, dd, J = 2.7, 17.0 Hz), 2.81 (1H, broad dd, J = 4.0, 7.1 Hz), 2.44 (1H, t, J = 2.7), 1.51 (3H, d, J = 7.1 Hz), 1.39 (1H, m), 1.03 (3H, d, J = 5.6 Hz), 1.01 (3H, d, J = 5.6 Hz); $^{13}$C NMR ($CDCl_3$) δ 114.03, 113.83, 76.06, 74.08, 47.84, 46.13, 40.85, 30.67, 28.53, 25.68, 23.10, 14.71; **6d-major** $^1$H NMR ($CDCl_3$) δ 4.18 (1H, dd, J = 2.4, 8.3 Hz), 3.10 (1H, dd, J = 2.6, 17 0 Hz), 2.96 (1H, dd, J = 2.6, 17.0 Hz), 2.40 (1H, t, J = 2.6 Hz), 2.03 (1H, broad dd, J = 2.4, 6.5 Hz), 1.89 (1H, m), 1.35 (3H, d, J = 6.6Hz), 1.17 (3H, d, J = 6.5 Hz), 1.04 (3H, d, J = 6.5 Hz); $^{13}$C NMR ($CDCl_3$) δ 114.03, 113.55, 75.76, 74.47, 46.36, 42.87, 40.02, 35.78, 27.27, 24.39, 20.35, 15.59.

**General Procedure for the Reductive Cyclization to Give 14.**

A solution of the iodide **6** (1.0 equiv) and tributyltin hydride (1.1 equiv) in degassed benzene (0.3 M) was refluxed for 4-10 h. The reaction mixture was diluted with wet ether (3x) and a solution of $I_2$ was added dropwise until the iodine color persisted. Then 1.2 equiv of DBU was added. The resulting mixture was filtered through silica gel and concentrated. Purification by column chromatography gave the cyclic compound **14**.

**1,1-Dicyano-4-butyl-3-(methylene)cyclopentane (14a).**

The reaction was conducted with iodide **6a** (100 mg, 0.32 mmol), tributyltin hydride (102 μL, 0.38 mmol), and AIBN (7 mg, 0.04 mmol) in refluxing benzene (3.2 mL) for 3 h. After DBU workup, purification by flash column chromatography (2% EtOAc in hexanes) afforded pure **14a** (42 mg, 69%) as a clear liquid: $^1$H NMR ($CDCl_3$) δ 5.12 (1H, m), 5.05 (1H, m), 3.15 (1H, dd, J = 15.3, 1.1 Hz), 3.01 (1H, dd, J = 15.3, 2.1 Hz), 2.70 (2H, m), 2.00 (1H,

dd, J = 13.2, 15.5 Hz), 1.72 (1H, m), 1.44-1.24 (5H, m), 0.90 (3H, t); $^{13}$C NMR ($CDCl_3$) δ 146.61 (s), 116.20 (s), 116.05 (s), 110.38 (t), 45.00 (t), 43.78 (d), 41.64 (t), 33.48 (s), 29.53 (t), 22.78 (t), 14.00 (q); IR (thin film) 3090, 2970, 2930, 2870, 2240, 1670, 1470, 890 cm$^{-1}$; LRMS (*m/e*) 188 ($M^+$), 187 ($M^+ - 1$), 173, 159, 147, 132, 119, 105, 91, 77, 68; HRMS calcd for $C_{12}H_{16}N_2$, 188.1099, found, 188.1099.

***trans*-1,1-Dicyano-4,5-dipropyl-3-(methylene)cyclopentane (14b).**

The reaction was conducted with the iodide **6b** (143 mg, 0.42 mmol), tributyltin hydride (123 μL, 0.46 mmol), and AIBN (10 mg, 0.06 mmol) in refluxing benzene (4.2 mL) for 6 h. After DBU workup, purification by flash column chromatography (8% EtOAc in hexanes) gave pure **14b** (54 mg, 59%) as a clear liquid: $^1$H NMR ($CDCl_3$) δ 5.13 (1H, dm, J = 2.5 Hz), 5.01 (1H, broad d, m, J = 2.5 Hz), 3.12 (1H, d, J = 16.8 Hz), 3.00 (1H, dq, J = 16.8, 2.5 Hz), 2.30 (1H, m), 2.26 (1H, m), 1.17 (2H, m), 1.58 (4H, m), 1.38 (2H, m), 1.01 (3H, t, J = 7.0 Hz), 0.93 (3H, t, J = 7.0 Hz); $^{13}$C NMR ($CDCl_3$) δ 146.06 (s), 116.52 (s), 114.29 (s), 110.93 (t), 53.64 (d), 47.26 (d), 45.49 (t), 37.83 (s), 35.73 (t), 34.13 (t), 21.02 (t), 19.22 (t), 14.29 (q), 14.28 (q); IR (thin film) 3080, 2960, 2940, 2870, 2250, 1670, 1460, 1390, 900, 760 cm$^{-1}$; LRMS (*m/e*) 216 ($M^+$), 201, 187, 174, 159, 148, 131, 120, 106, 96; HRMS calcd for $C_{14}H_{20}N_2$, 216.1622, found, 216.1626.

***trans*-1,1-Dicyano-5-methyl-4-phenyl-3-(methylene)cyclopentane (14c).**

The reaction was carried out with the iodide **7c** (175 mg, 0.50 mmol), tributyltin hydride (148 μL, 0.55 mmol) and AIBN (10 mg, 0.06 mmol) in refluxing benzene (3.2 mL) for 9 h. After DBU workup, purification by flash column chromatography (8% EtOAc in hexanes) afforded pure **14c** (91 mg, 82%) as a clear liquid: $^1$H NMR ($CDCl_3$) δ 7.36 (3H, m), 7.18 (2H, m), 5.20 (1H, m), 4.75 (1H, m), 3.44 (1H, d, J = 17.3 Hz), 3.42 (1H, dd, J = 9.5, 2.7 Hz), 3.29 (1H, dq, J = 17.3, 2.7 Hz), 2.58 (1H, dd, J = 6.2, 9.4 Hz), 1.28 (3H, d, J = 6.5 Hz); $^{13}$C NMR ($CDCl_3$) δ 146.29 (s), 139.27 (s), 129.02 (d), 128.68 (d), 127.75 (d), 115.52 (s), 114.26 (s), 113.03 (t), 55.55 (d), 52.44 (d), 44.16 (t), 39.17 (s), 13.59 (q); IR (thin film) 3095, 3040, 2980, 2940, 2890, 2240, 1670, 1620, 1490, 1460, 1390, 1090, 910, 760, 710 cm$^{-1}$; LRMS (*m/e*) 222 ($M^+$), 207, 197, 182, 169, 154, 143, 130, 115, 102, 91, 77, 65; HRMS calcd for $C_{15}H_{14}N_2$, 222.1154, found, 222.1157.

***trans*-1,1-Dicyano-5-methyl-4-isopropyl-3-(methylene)cyclopentane (14d).**

The reaction was performed with the iodide **6d** (86 mg, 0.27 mmol), tributyltin hydride (81 μL, 0.30 mmol), and AIBN (7 mg, 0.04 mmol) in refluxing benzene (2.6 mL) for 4 h. After DBU workup, purification by flash column chromatography (8% EtOAc in hexanes) produced pure **14d** (36 mg, 76%) as a clear liquid: $^1$H NMR ($CDCl_3$) δ 5.21 (1H, m, J = 1.0 Hz), 5.05 (1H, broad d, J = 2.5 Hz), 3.06 (1H, dt, J = 15.8, 1.0 Hz), 2.87 (1H, dq, J = 15.8, 2.5 Hz), 2.45 (1H, dd, J = 6.5, 6.5 Hz), 2.24 (1H, m), 1.93 (1H, m), 1.42 (3H, d, J = 6.8 Hz), 0.98 (3H, d, J = 6.8 Hz), 0.96 (3H, d, J = 6.8 Hz); $^{13}$C NMR ($CDCl_3$) δ 145.05 (s), 115.84 (s), 114.22 (s), 112.38 (t), 53.50 (d), 47.13 (d), 45.83 (t), 30.50 (s), 19.50 (q), 19.31 (q), 16.46 (q); IR (thin film) 3090, 2980, 2940, 2890, 2250, 1680, 1470, 1400, 910 cm$^{-1}$; LRMS (*m/e*) 188 ($M^+$), 146, 131, 118, 106, 91, 73; HRMS calcd for $C_{12}H_{16}N_2$, 188.1310, found, 188.1315.

***cis*-1,1-Dicyano-3-(methylene)bicyclo[3.3.0]octane (14e).**

The reaction was performed with iodide **6e** (100 mg, 0.34 mmol), tributyltin hydride (108 μL, 0.40 mmol), and AIBN (8 mg, 0.05 mmol) in refluxing benzene (3.2 mL) for 3 h. After DBU workup, purification by flash column chromatography (4% EtOAc in hexanes) gave pure **14e** (48 mg, 83%) as a clear liquid: $^1$H NMR ($CDCl_3$) δ 5.14 (1H, m, J = 2.6 Hz), 5.06 (1H, broad d, J = 2.6 Hz), 3.16 (1H, m), 3.12 (1H, m), 3.02 (2H, d, J = 2.6 Hz), 2.05 (2H, m), 1.72 (2H, m), 1.67 (2H, m); $^{13}$C NMR ($CDCl_3$) δ 147.86 (s), 116.52 (s), 115.07 (s), 111.38 (t), 53.54 (d), 47.26 (d), 44.45 (t), 37.40 (s), 34.33 (t), 30.47 (t), 26.59 (t); IR (thin film) 3090, 2970, 2940, 2880, 2250, 1670, 1480, 1460, 1280, 1130, 910; LRMS (*m/e*) 172 ($M^+$), 157, 144, 130, 117, 104, 94, 79, 67, 56 cm$^{-1}$; HRMS calcd for $C_{11}H_{12}N_2$, 172.0998, found, 172.1000.

***cis*-1,1-Dicyano-3-(methylene)bicyclo[4.3.0]nonane (14g).**

The reaction was conducted with the iodide **6g** (120 mg, 0.38 mmol), tributyltin hydride (124 μL, 0.46 mmol)

and AIBN (8 mg, 0.05 mmol), in refluxing benzene (2.5 mL) for 6 h. After DBU workup, purification by flash column chromatography (8% EtOAc in hexanes) afforded pure **14g** (57 mg, 79%) as a clear liquid: $^1$H NMR ($CDCl_3$) δ 5.15 (1H, m,), 5.04 (1H, m), 3.27, (1H, d, J = 17.5 Hz), 3.12 (1H, dq, J = 17.5, 2.5 Hz), 2.98 (1H, m), 2.61 (1H, dt, J = 5.5, 12.3 Hz), 2.03 (1H, m), 1.93 (1H, m), 1.82 (1H, m), 1.68 (1H, m), 1.47 (1H, m), 1.26 (2H, m), 1.04 (1H, m); $^{13}$C NMR ($CDCl_3$) δ 143.25 (s), 116.65 (s), 114.65 (s), 109.40 (t), 48.23 (d), 41.98 (t), 41.51 (d), 36.15 (s), 24.85 (t), 24.42 (t), 24.28 (t), 19.80 (t); IR (thin film) 3090, 2940, 2860, 2250, 1670, 1250, 1110, 910 cm$^{-1}$; LRMS (*m/e*) 186 ($M^+$), 158, 144, 132, 118, 108, 93, 79, 67; HRMS calcd for $C_{12}H_{14}N_2$, 186.1154, found, 186.1157.

***cis*-1,1-Dicyano-9-methyl-3-(methylene)bicyclo[4.3.0]nonane (14h).**

A solution of iodomalononitrile **1** (300 mg, 1.30 mmol) and 1-methylcyclohexene (308 μL, 2.61 mmol) in degassed benzene (6.5 mL) was heated for 24 h at 80 °C in the dark. The reaction mixture was diluted with ether (20 mL), filtered through silica gel, and concentrated to produce the crude iodide **6h** (305 mg, 72%). The subsequent reductive cyclization was initiated by addition of tributyltin hydride (350 μL, 1.30 mmol) and AIBN (21 mg, 0.13 mmol) to the solution of the crude iodide in benzene (4.3 mL). After refluxing for 6 h, the resulting mixture was diluted with ether (20 mL), treated with 1.2 equiv of DBU at room temperature, and filtered through silica gel. Evaporation of solvent and purification by column chromatography (10% EtOAc in hexanes) gave **14h** (117 mg, 45%): $^1$H NMR ($CDCl_3$) δ 5.06 (1H, m), 4.97 (1H, m), 3.17 (2H, m), 2.33 (1H, t, J = 6.8 Hz), 1.98-1.76 (2H, m), 1.74-1.54 (2H, m), 1.52-1.36 (4H, m), 1.26 (3H, s); $^{13}$C NMR ($CDCl_3$) δ 151.74 (s), 117.49 (s), 116.29 (s), 108.28 (t), 54.25 (d), 44.35 (s), 43.55 (t), 35.67 (s), 34.69 (t), 28.27 (q), 24.65 (t), 21.87 (t), 20.83 (t); IR (thin film) 3090, 2940, 2870, 2250, 1460, 910 cm$^{-1}$; LRMS (*m/e*) 200 ($M^+$), 185, 173, 158, 144, 131, 122, 107, 93, 79, 67; HRMS for $C_{13}H_{16}N_2$, 200.1310, found, 200.1313.

**(*cis/anti/cis*)-3,3-Dicyano-1-(methylene)tricyclo[6.3.0.0]undecane; and (*cis/anti/cis*)-1,1-Dicyano-3-(methylene)tricyclo[6.3.0.0]undecane, (14i/14j).**

A solution of iodomalononitrile **1** (300 mg, 1.30 mmol) and *cis*-bicyclo[3.3.0]oct-2-ene (237 μL, 1.95 mmol) in degassed benzene (6.5 mL) was heated for 12 h at 80 °C in the dark. The reaction mixture was diluted with ether (320 mL), filtered through silica gel, and concentrated to give a 1.5:1 mixture of the crude iodides **6i** and **6j** as a clear oil: **6i** $^1$H NMR ($CDCl_3$) δ 4.18 (1H, dd, J = 7.8, 8.9 Hz), 3.94 (1H, m), 3.26 (2H, d, J = 2.8 Hz), 3.16 (1H, dd, J = 16.9, 2.8 Hz), 2.94 (1H, dd, J = 2.6, 7.6 Hz), 2.78 (1H, m), 2.68-2.36 (2H, m), 2.18 (1H, m), 2.06-1.34 (6H, m); **6j** $^1$H NMR ($CDCl_3$) δ 4.30 (1H, ddd, J = 2.4, 7.6, 13.5 Hz), 3.08 (2H, d, J = 2.8 Hz).

The subsequent reductive cyclization of **6i/6j** was conducted by addition of tributyltin hydride (385 μL, 1.43 mmol) and AIBN (28 mg, 0.17 mmol) to the solution of the crude iodides in benzene (4.3 mL). After refluxing for 3 h, the resulting mixture was diluted with ether (20 mL), treated with DBU ( 297 μL, 1.95 mmol) and $I_2$, and filtered through silica gel. Evaporation of solvent and purification by column chromatography (2% EtOAc in hexanes) gave an inseparable 1.5:1 mixture of **14i** and **14j** (223 mg, 81%) as a clear liquid: $^1$H NMR ($CDCl_3$) δ 5.14 (3H, m), 5.07 (1H, m), 3.18 (2H, m), 3.13 (4H, d), 2.89 (1H, m), 2.74 (1H, m), 2.67 (2H, m), 2.56 (1H, m), 2.45 (1H, m), 2.05 (1H, m), 1.96-1.78 (5H, m), 1.76-1.46 (7H, m), 1.44-1.24 (3H, m); $^{13}$C NMR ($CDCl_3$) δ 147.94 (s), 146.89 (s), 116.68 (s), 116.59 (s), 115.42 (s), 114.75 (s), 111.26 (t), 111.12 (t), 61.66 (d), 55.30 (d), 54.25 (d), 52.38 (d), 49.56 (d), 47.75 (d), 44.42 (d), 44.23 (d), 44.13 (t), 43.44 (t), 39.98 (t), 37.01 (s), 36.01 (s), 35.92 (t), 34.42 (t), 33.74 (t), 33.48 (t), 32.84 (t), 26.52 (t), 25.82 (t); IR (thin film) 2980, 2940, 2240, 1650, 1460, 1370, 1080, 960 cm$^{-1}$; LRMS (*m/e*) 212 ($M^+$), 197, 184, 169, 157, 134, 119, 107, 91, 67; HRMS calcd $C_{14}H_6N_2$, 212.1316, found, 212.1316.

**1-Cyano-4-butyl-3-oxocyclopent-1-ene (16).**

Compound **16** was prepared by the procedure given below for **17**. Ozonolysis of the dicyano exo-methylene cyclopentane **14a** (0.2 g, 1.05 mmol) was followed by treatment with excess DBU (0.32 mL, 2.12 mmol) in THF (10 mL) at 25°C to afford a β-cyano enone **16** (0.14 g, 82 %) as a clear liquid: $^1$H NMR ($CDCl_3$) δ 7.12 (1H, s), 3.80 (1H, m), 2.85 (1H, dd, J = 7.2, 18.8 Hz), 2.68 (1H, dd, J = 3.3, 18.8 Hz), 2.22 (2H, m), 1.48 (2H, m), 1.36 (2H, m), 0.90 (3H, t, J = 6.9 Hz); $^{13}$C NMR ($CDCl_3$) δ 203.82 (s), 149.49 (s), 148.16 (d), 118.66 (s), 38.41 (t), 29.34 (t),

27.88 (d), 24.48 (t), 22.41 (t), 13.78 (q); IR (thin film) 3090, 2970, 2940, 2870, 2260, 1720, 1470, 1060, 960 $cm^{-1}$; LRMS (*m/e*) 163 ($M^+$), 148, 134, 121, 109, 93, 79, 65, 51; HRMS calcd for $C_{10}H_{13}NO$, 163.0992, found, 163.0992.

**cis-1-Cyano-3-oxobicyclo[3.3.0]oct-1-ene (17).**

Compound **14e** (200 mg, 1.16 mmol) was dissolved in $CH_3OH$-$CH_2Cl_2$ (20 mL, 1:3 ratio) and cooled to –78 °C. Ozone was bubbled into the reaction mixture until the color of the solution remained blue. Next, oxygen was bubbled through the reaction mixture to remove excess ozone. After addition of excess $(CH_3)_2S$, the reaction mixture was warmed to 25°C and stirred for 12 h. The resulting solution was diluted with ether (60 mL), washed with water and brine, and concentrated under reduced pressure to give the crude ketone: $^1H$ NMR ($CDCl_3$) δ 3.37 (1H, dt, J = 8.7, 8.2 Hz), 3.08 (1H, dd, J = 13.7, 1.1 Hz), 2.97 (1H, dt, J = 8.7, 4.2 Hz), 2.95 (1H, d, J = 13.7 Hz), 2.24 (1H, m), 2.04 (2H, m), 1.76 (2H, m), 1.66 (1H, m); $^{13}C$ NMR ($CDCl_3$) δ 210.95 (s), 115.89 (s), 114.23 (s), 51.50 (d), 50.46 (d), 45.66 (t), 32.80 (s), 30.25 (t), 29.70 (t), 25.84 (t); IR (thin film) 2975, 2930, 2890, 2260, 1765, 1280, 1120 $cm^{-1}$; LRMS (*m/e*) 174 ($M^+$), 156, 145, 130, 119, 106, 96, 78, 68, 55; HRMS calcd for $C_{10}H_{10}N_2O$, 174.0793, found, 174.0793.

The crude ketone was dissolved in THF (8 mL) and treated with excess DBU for 1 h at room temperature. The reaction mixture was diluted with ether (30 mL), and washed with water (2 x 20 mL) and brine (2 x 10 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, 20% EtOAc in hexanes) afforded 148 mg (87%) of pure **17**: $^1H$ NMR ($CDCl_3$) δ 6.66 (1H, s), 3.49 (1H, dt, J = 6.7, 2.6 Hz), 2.84 (1H, broad dd, J = 1.7, 5.9 Hz), 1.78 (5H, m), 1.25 (1H, m); $^{13}C$ NMR ($CDCl_3$) δ 209.94 (s), 146.16 (s), 143.15 (d), 114.73 (s), 50.14 (d), 48.16 (d), 30.37 (t), 29.08 (t), 23.51 (t); IR (thin film) 3090, 2980, 2880, 2230, 1730, 1710, 1610, 1460, 1290, 1180, 1090, 1930, 910, 650 $cm^{-1}$; LRMS (*m/e*) 147 ($M^+$), 119, 106, 91, 78, 67, 59; HRMS calcd for $C_9H_9NO$, 147.0682, found, 147.0684.

**(cis/anti/cis)-11-Cyano-5-oxo-3-(methylene)tricyclo[6.3.0.0]undecane (19).**

A solution of β-cyano bicyclic enone **17** (40 mg, 0.27 mmol), 4-iodo-1-butyne (58 mg, 0.32 mmol), and hexabutylditin (16 μL, 0.03 mmol) in benzene (1 mL) was irradiated with a GE-275W sunlamp at 80-85 °C for 40 min. After evaporation of the solvent, the residue was purified by flash chromatography (10% EtOAc in hexanes) to afford the inseparable mixture of the vinyl iodides **18E** and **18Z** (71 mg, 81% combined yield). The mixture was exposed to the standard tin hydride reduction with tributyltin hydride (59 μL, 0.24 mmol) and AIBN (4 mg) in benzene (1 mL). After refluxing for 6 h, the reaction mixture was concentrated. The residue containing tin species was recrystallized (100% hexane) to give **19** (40 mg, 75% overall yield from the enone **17**) as white crystals (mp 71-72 °C): $^1H$ NMR ($CDCl_3$) δ 5.43 (1H, m), 5.30 (1H, m), 3.03 (1H, dd, J = 6.8, 1.0 Hz), 2.87 (1H, dt, J = 8.2, 8.1 Hz), 2.58 (2H, m), 2.31-2.14 (3H, m), 2.10 (1H, m), 1.96 (2H, m), 1.64 (3H, m); $^{13}C$ NMR ($CDCl_3$) δ 219.98 (s), 151.95 (s), 121.83 (s), 112.10 (t), 57.98 (d), 52.61 (d), 50.52 (d), 49.24 (s), 32.58 (t), 31.99 (t), 30.02 (t), 27.76 (t), 26.02 (t); IR (thin film) 3090, 2970, 2920, 2880, 2260, 2740, 1670, 1460, 1300, 1130, 910, 730 $cm^{-1}$; LRMS (*m/e*) 201 ($M^+$), 173, 156, 142, 128, 105, 96, 88, 67. The DBU workup must be avoided for this reaction, otherwise, an unknown new product is formed.[27] A control experiment (see below) showed that this product resulted form the DBU treatment and not the radical annulation.

**Unknown product from treatment of 19 with DBU.[27]**

Pure **19** (40 mg, 0.20 mmol) was dissolved in THF (4 mL) and treated with excess DBU (61 μL, 0.40 mmol) for 12 h. The reaction mixture was filtered through silica gel pad and concentrated to afford the crude mixture of unknown and recovered starting material **19** in the ratio of 1.00:0.65. The crude mixture was purified by semi-preparative HPLC (5% EtOAc in hexanes) to give pure unknown (11mg) as white crystals: $^1H$ NMR ($CDCl_3$) δ 5.59 (1H, m), 5.41 (1H, m), 3.39 (1H, dd, J = 7.5, 9.6 Hz), 2.78 (1H, m), 2.60 (1H, m), 2.59-2.44 (4H, m), 2.37 (1H, m), 2.26 (1H, m), 2.06 (1H, m), 1.96 (1H, m); IR (thin film) 3090, 3030, 2940, 2240, 1740, 1450, 1210, 1130, 910 $cm^{-1}$; MS (*m/e*) 199 ($M^+$), 171, 156, 132, 104, 95, 77, 67.

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| Reaction Time | Syn/Anti Ratio of 6c | Ratio 6c/7c |
|---|---|---|
| 0.5 | 10.2 | (–)[a] |
| 1 | 7.2 | (–)[a] |
| 2 | 6.0 | 0.10 |
| 4 | 4.4 | 0.13 |
| 8 | 1.5 | 0.33 |
| 9 | 1.4 | 0.37 |
| 11.5 | 1.0 | 0.75 |
| 18 | 0.9 | 4.43 |
| 20 | 0.8 | 6.00 |

a) **7c** could not be detected.


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