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More on Adamantene[†,1]

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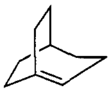
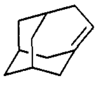
Abstract: At high dilution and temperature adamantene undergoes a retro Diels−Alder cycloaddition to a triene, as well as retro-insertion reactions to give carbenes. 1,2-Diiodoadamantane and 3-diiodomethylnoradamantane react with methyllithium in the gas phase to give adamantene, which is efficiently reduced to adamantane under these conditions. Addition of adamantene to butadiene occurs in 4 + 2 and 2 + 2 fashion.

Since Bredt pointed out in 1924 that double bonds did not appear at the bridgehead positions of the pinane and camphane bicyclic systems,[2] chemists have turned their energies to finding ways to violate "Bredt's rule", and myriad bridgehead alkenes of varying stability have been described.[3] Several generalizations of their behavior have appeared, early on most notably by Prelog,[4] Fawcett,[5] Köbrich,[6] and Wiseman.[7] In 1981 Maier and Schleyer defined a most useful measure of stability, "olefinic strain" (OS), as the difference between the total strain energy of the most stable conformer of the parent hydrocarbon and the total strain energy of the most stable conformer of the bridgehead alkene.[8] This led to three empirically generated categories: (a) isolable bridgehead alkenes with OS $\leq$ 17 kcal/mol; (b) observable bridgehead alkenes with OS between 17 and 21 kcal/mol; and (c) unstable bridgehead alkenes in which OS $\geq$ 21 kcal/mol. Many only slightly strained, and thus more or less normal, class (a), bridgehead alkenes are now known.[3] Typical of group (b) are homoadamantene[9] and bicyclo[3.2.2]non-1-ene,[10] with OS values of 20.2 and 19.5 kcal/mol, respectively. Each of these alkenes is observable, but only at low temperature. Olefins in catagory (c) were expected to be observable only under matrix conditions, if then.[8] Solidly in this group lies the subject of this paper, adamantene (**1**), with a heat of formation calculated to be 32.36 kcal/mol, and an OS of 39.5 kcal/mol.[8] The twist angle between the orbitals making up the π portion of the double bond has been estimated at 64°.[11]


OS = 19.5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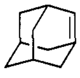
1, OS = 39.5

Adamantene has a long and sometimes contradictory history. Several very early attempts at synthesis ended in failure.[12] In 1972, however, the isolation of cyclobutane (2 + 2) dimers of adamantene on treatment of 1,2-dihaloadamantanes with alkyllithium reagents was reported by the groups of McKervey[13] and Lenoir.[14] It was specifically noted by both groups that furan was an ineffective trap for adamantene. Only a year later a new route to adamantene, Wynberg's thermal decomposition of adamantane-1,2-di-*tert*-butyl perester was reported, and this "adamantene" did add to 2,5-dimethylfuran, albeit in low yield.[15] Compelling evidence for adamantene appeared in the Norish type II cleavage of adamanyl esters, as the same alcohol-trapped products were formed from both 1- and 2-substituted adamantanes.[16] McKervey,[17] and others,[18] next countered Wynberg's suggestion that there was something amiss with the dihaloadamantane route to adamantene by showing that butadiene, if not furan, did react with **1** to give a Diels−Alder product.

Conflicting reports over the addition to furans continued to appear in later years. For example, Lenoir used an electrochemical method to dehalogenate 1,2-dihaloadamantanes and isolated dimers of adamantene and Diels−Alder adducts with butadiene, cyclopentadiene, and furan.[19] Debromination of 1,2-dibromoadamantane with bis(trimethylsilyl)mercury likewise led to an adduct with furan.[20] On the other hand, metal phosphides failed to give furan adducts when they were used to dehalogenate 1,2-dihaloadamantanes.[18]

[†] It gives us great pleasure to dedicate this paper to Professor Manfred Regitz on the occasion of his 60th birthday.

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(1) We thank the National Science Foundation for support for this work through grants CHE 9024996 and CHE 9322579.

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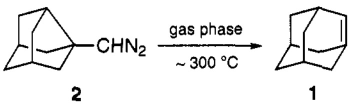
Attempts at low-temperature isolation led to infrared or Raman spectra of varying quality.[11,21] The best of these showed a band in the Raman at 1481 cm^{-1} for adamantene.[11]

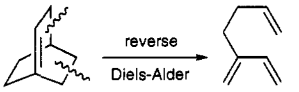
In 1978, we introduced a new method for generating adamantene, the ring expansion of 1-noradamantyldiazomethane (**2**). Unfortunately, our experiments were confined to the gas phase. We found the cyclobutane dimers were able to trap adamantene with butadiene and uncovered the first hints of diradical character in the formation of 1,1′-, 1,2′-, and 2,2′-biadamantyl.[22]



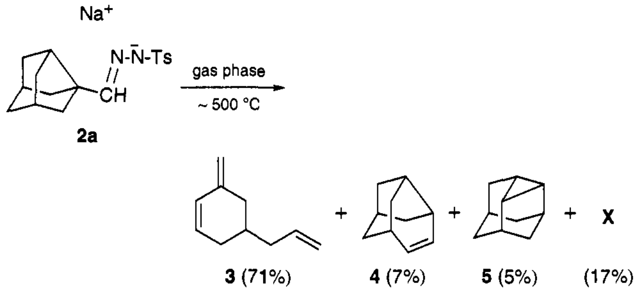
So, the situation was complex: adamantene made from different sources either did or did not add to furans. Clearly, some of the routes to "adamantene" were in fact only mimicking adamantene. Given the many examples of metal- or base-induced dehalogenations, our prejudice was in favor of the alkyllithium-induced dehalogenations leading to a real adamantene. However, the organometallic route is not above suspicion. Organolithium reagents promote coupling of haloadamantanes,[23] and the cyclobutane dimers could easily have been formed through such a process. Certainly, were the simple McKervey dehalogenation in solution to really involve adamantene, the lives of those studying its properties would be easier. We hoped to forge a better link between adamantene generated by butyllithium-induced dehalogenations in solution and that made in the gas phase through carbene (or diazo compound) ring expansion.

In this paper we amplify our earlier report,[22] fill gaps in it and some other early papers, and report two new routes to adamantene. In addition, we add to the list of remarkable reactions of adamantene and present evidence that makes it likely that McKervey's alkyllithium route does produce adamantene. Our strategy was to find reactions diagnostic of "real" adamantene and see if the McKervey dehalogenation route also produced them.

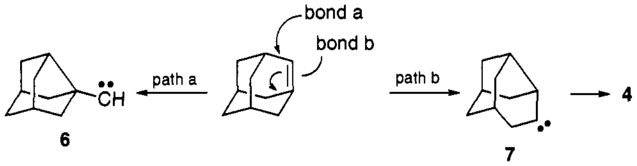
What gaps exist in our (and others') reports on adamantene? First of all, adamantene is a cyclohexene, and at high temperature it might well be expected to escape its twisted existence through a reverse Diels–Alder cycloaddition to give **3**. Related bridgehead cyclohexenes such as bicyclo[2.2.2]oct-1-ene undergo exactly that kind of reaction.[24] It seems odd that the analogous reaction of **1** was not found earlier by us[22] or others. We are able to reproduce the products described earlier (300 °C)[22] by decomposing tosylhydrazone salt **2a** in a static system at 460 °C/0.05 Torr, but find in a flowing system at 500 °C/ <0.001 Torr the expected product of reverse Diels–Alder reaction, **3**, along with **4**, **5**, and an unknown compound, **X**.[25]



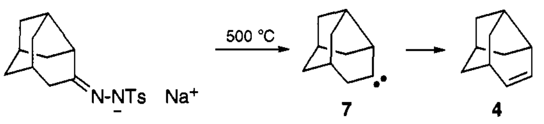
So, the simple expedients of decreasing the pressure and slightly increasing the temperature serve to reveal the missing reverse Diels–Alder reaction and to uncover products of new unimolecular reactions of **1**.



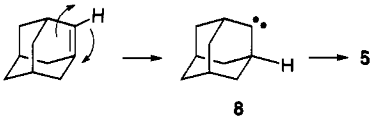
What are the sources of **4** and **5**? Generally, the carbon–carbon insertion reaction of an alkylcarbene to give a simple alkene can be expected to be so exothermic as to make the reverse process unthinkable. However, were the energy of the alkene product to be raised, as it is in twisted alkenes, eventually the reverse process becomes not only possible but inevitable. For example, in 1991, we and the Platz group described a carbene-bridgehead alkene pair in equilibrium.[26] We suspect that similar reactions of adamantene lead to **4** and **5**. Adamantene can revert to a carbene in two ways. One, path a (retro-insertion into carbon–carbon bond a), merely generates carbene **6**, but the other, path b (retro-insertion into carbon–carbon bond b), leads to **7**, the likely source of **4**.



Alkene **4** is known,[27] and we have verified that FVP of the sodium salt of the tosylhydrazone of tricyclo[4.3.1.$0^{3,8}$]dec-4-one leads only to **4**.



Compound **5** might be formed through a similar process in which a reverse carbon–hydrogen insertion leads to carbene **8**, a species known to form **5**.[28]



In earlier work on 1-norbornyldiazomethane we noted that ring expansion took place only through the shorter bridge.[24] That appears to be the case with **6** as well. Ring expansion through the longer bridge would lead to **9**, and reverse Diels–Alder reaction would generate **10**. We have shown through indepen-

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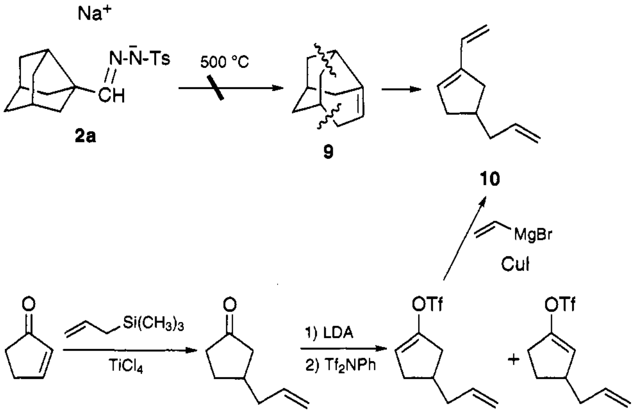
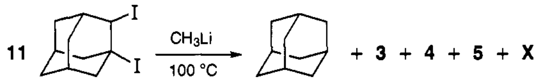
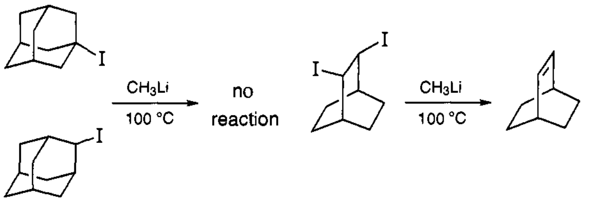
dent synthesis that **10** is absent from the products when **2a** is decomposed at 500 °C.



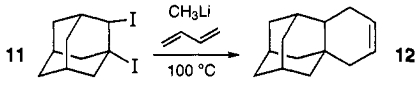
Adamantene has been approached many times through **11** and related 1,2-dihaloadamantanes.[13,14,16-21] As discussed earlier, these attempts are bedeviled by discrepancies in the properties of adamantene reported for different methods of generation. There is a strong possibility that some of the reactions of **11** are organometallic mediated and have little or nothing to do with adamantene. Indeed, it seems that this must be so. However, the most simple of these reactions, the original McKervey route in which 1,2-diiodoadamantane is treated with butyllithium at low temperature, remains a strong candidate for a source of real adamantene. We set out to decompose **11** in the "gas phase" using the methyllithium technique pioneered by Brinker,[29] and borrowed by us on an earlier occasion.[30] Even at the 100 °C limit imposed by the stability of methyllithium, we see traces of the products of unimolecular decomposition of adamantene, **3**, **4**, **5**, and **X**. By far the major product, however, is adamantane (at 60% conversion of **11** about 70% of product is adamantane).



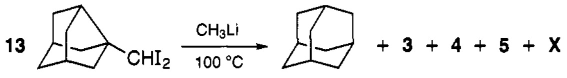
A series of control experiments shows that adamantane is a product of reduction of adamantene, and not the result of sequential replacement of the two iodines with hydrogen. Both 1- and 2-iodoadamantane pass through our apparatus essentially unscathed; only traces of adamantane are formed. However, simple 1,2-diiodides are transformed into alkenes under our conditions. Thus, *trans*-2,3-diiodobicyclo[2.2.2]octane produces bicyclo[2.2.2]oct-2-ene efficiently (90% conversion, <0.1% reduction to bicyclo[2.2.2]octane). It appears that normal alkenes are not reduced under these conditions, whereas the highly twisted adamantene is.



When **11** is swept into the methyllithium tube with a stream of butadiene, adamantane is no longer formed, but small amounts of the known adduct **12** are produced. We cannot yet comment on the mechanism of reduction beyond noting that when CD_3Li is used, adamantane-d_0, -d_1, and -d_2 are all formed (ratio: 50:38:12).



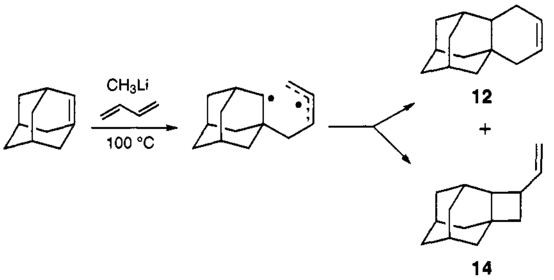
Another potential source of carbene **6**, and of adamantene, is diiodide **13**. This molecule also forms adamantane, along with traces of **3**, **4**, **5**, and **X**, when passed through the methyllithium tube.



To sum up: at high dilution and temperature adamantene undergoes a reverse Diels–Alder reaction to give **3** as well as reversion to carbenes **7**, **8**, and probably **6**. Diiodides **11** and **13** form adamantene on reaction with methyllithium at 100 °C. Under these conditions the highly twisted adamantene is predominantly reduced to adamantane, but the products of unimolecular reaction appear as well.

What can we say about McKervey's solution route? We have shown that methyllithium is capable of generating adamantene from 1,2-diiodoadamantane in the Brinker methyllithium tube. This does not absolutely mean that adamantene is formed *in solution* from 1,2-diiodoadamantane and butyllithium, but it surely makes this a reasonable supposition. A sensible next step would be to show that the methyllithium tube and alkyllithium in solution give the same mixture of products in a variety of reactions.

We can provide one final new reaction of adamantene. Several times adamantene has been trapped through Diels–Alder reaction with butadiene to give **12**.[17,19,22] However, there is another product, the vinylcyclobutene **14**, formed in about 7% of the major isomer. That **14** is a vinyl compound is clear from the simple ^1H NMR spectrum [typical vinyl signals at δ 5.87 (1H) and 5.0–5.1 (2H)]. Two proton-selective decoupling experiments and a DQ-COSY NMR experiment show that the single tertiary hydrogen adjacent to the vinyl group is coupled to three hydrogens, not two, Thus the regiochemistry is correct as shown. The formation of this 2 + 2 adduct is consistent with the notion that adamantene is no normal alkene and, in particular, undergoes stepwise additions to dienes. It remains to be seen how much of the 2 + 4 adduct, the Diels–Alder adduct **12**, derives from the stepwise path. An investigation of the stereochemistry of the Diels–Alder and 2 + 2 reaction is underway.



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Our results with the methyllithium tube show that adamantene is formed under these rather odd conditions and reveal the nature of the unimolecular reactions of this highly twisted alkene. More important, perhaps, they increase our confidence that adamantene is also formed in solution as well, under the related but much more conventional conditions of McKervey.

Experimental Section

General. All chemicals were purchased from Aldrich Chemical Co. except as indicated or were synthesized as described. ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250, GE QE-300, JEOL GSX-270, and JEOL GSX-500 instruments. In most cases, $CDCl_3$ was used as solvent for NMR analysis and the residual $CHCl_3$ in $CDCl_3$ was taken as the internal standard. The chemical shift of the $CHCl_3$ proton was set at 7.24 ppm, and the central peak of the $CDCl_3$ carbon was set at 77.0 ppm. ^{1}H homonuclear selective decoupling experiments were conducted on the JEOL GSX-270 machine. The ^{1}H DQ-COSY NMR experiment was also recorded on the JOEL GSX-270 machine. GC/MS analyses were carried out on a Hewlett-Packard 5890/5971 gas chromatograph-mass selective detector with a 0.2 mm i.d., 0.33 μm film thickness, 25 m HP-1 capillary column. Preparative gas chromatographic separations were performed on a Gow-Mac series 580 gas chromatograph with helium as carrier gas. The 6 ft × 0.25 in. columns were constructed of either 10% OV-101 or 10% SP-2100 silicon oil absorbed on 80/100 mesh Chromosorb WHP. IR spectra were taken on a Nicolet 5DBX spectrometer.

General Procedure for Flash Vacuum Pyrolysis. The furnace was constructed by wrapping a 115 mm × 12 mm quartz tube with 24 gauge Nichrome wire. The tube was insulated with Fiberfrax and was attached through a 14/20 ground glass joint to a round-bottomed flask that contained starting material. The other end of the furnace was connected to the vacuum line through a trap containing a cold finger. Tosylhydrazone sodium salt was synthesized by injecting a THF solution of the tosylhydrazone to 1.1 equiv of NaH (60%, in mineral oil). The reaction was carried out under Ar, and THF was driven out by flowing Ar. The dry sodium salt was obtained within 8 h and it was used directly for the FVP. Usually the same flask that the sodium salt was formed in could be used for FVP. When the desired vacuum was achieved, the valve that connected the sodium salt to the vacuum system was opened. The sodium salt was heated by an air bath to ca. 90 °C. The hot tube (furnace) was heated up at the same time by setting it to the desired temperature. The furnace was pre-calibrated by a thermocouple and the temperature was controlled by a Variac. Liquid nitrogen was filled into the cold finger of the trap as the temperature rose. White solids (sometimes faint yellow solids) condensed on the cold finger within ca. 20 min. The reaction usually took 40−60 min. Then, vacuum was released and the white solids could be rinsed off by the appropriate solvent.

FVP of Tosylhydrazone Sodium Salt (2a). Pyrolysis Under "Dimer-Forming" Conditions. About 400 mg of freshly made tosylhydrazone sodium salt was placed in a solids addition device which was attached to one neck of a hot quartz flask. The other neck of the hot flask was connected to a liquid-nitrogen-cooled trap which was connected to the vacuum (ca. 0.05 Torr). The hot flask temperature was calibrated and controlled through a Variac. When the hot flask was heated to 460 °C, the tosylhydrazone sodium salt in the addition finger was dropped in small portions to the hot surface. After about 0.5 h, the reaction was finished and products in the trap were analyzed by GC/MS.

FVP of Tosylhydrazone Sodium Salt (2a). Pyrolysis Under Monomer-Forming Conditions. About 400 mg of freshly made tosylhydrazone sodium salt (**2a**) was placed in a round-bottom flask connected to the hot tube. As the hot tube temperature reached 500 °C, the sodium salt was heated by an air bath of 80−90 °C under a vacuum of 0.001 Torr. A white solid was condensed on the cold finger. When the reaction was finished, the solid was rinsed off with $CDCl_3$ and subjected to a GC/MS analysis.

Compound 3: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.12 (d, J = 10 Hz, 1H), 5.77 (m, 2H), 5.02 (d, J = 20 Hz, 1H), 5.01 (d, J = 13 Hz, 1H), 4.77 (s, 1H), 4.73 (s, 1H), 1.6−2.5 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 136.8, 129.40, 129.35, 115.9, 110.8, 40.3, 36.7, 33.8, 31.5. MS, *m/e* (rel intensity) 134 (20), 119 (12), 105 (15), 93 (95), 91 (100), 77 (78), 65 (20). HRMS cacld for $C_{10}H_{14}$ (M^+) 134.1095, found 134.1098.

Synthesis of 5. To a THF solution of the tosylhydrazone of 2-adamantanone (1 g, 3.14 mmol) was added 1.26 mL of BuLi solution (2.5 M in THF, 3.14 mmol) at 0 °C. The solution turned orange. Argon was blown through the reaction flask until all the THF was carried out. The dry lithium salt was heated on an oil bath to 130~140 °C. A white solid was condensed on the upper part of the flask and collected. Analysis by ^{1}H NMR spectroscopy showed that it was tetracyclo-[3.3.1.1^{3,7}.0^{2,4}]decane (**5**): mp 201−202 °C (lit.[31] mp 202.5−203.5 °C). ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.25 (br, 2H), 2.12 (m, 1H), 1.81 (s, 3H), 1.3−1.5 (m, 7H), 1.2 (m, 1H).

Synthesis of 4. The tosylhydrazone of tricyclo[4.3.1.0^{3,8}]dec-4-one[27] (1 g, 3.14 mmol) in dry THF was cooled to 0−5 °C. To this solution was added 5 mL of BuLi (2.5 M in THF). A dark green solution was formed. This solution was stored at room temperature for 48 h. The mixture was cooled, diluted with ice−water, acidified, and extracted three times with 20 mL of ether. The orange ether layers were combined and washed successively with 30 mL of an aqueous solution of 10% Na_2CO_3, water, and saturated brine and dried over Na_2SO_4. After the solvent was removed by rotary evaporation, the crude product was further purified by sublimation to give a white solid, tricyclo-[4.3.1.0^{3,8}]dec-4-ene (**4**): mp 184−185 °C (lit.[32] mp 183−185 °C). ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.18 (m, 2H), 2.65 (m, 1H), 2.2−2.4 (m, 3H), 1.4−1.8 (m, 8H).

Synthesis of 10. 1,4-Addition of Allyltrimethylsilane to 2-Cyclopenten-1-one. To a 100-mL, three-necked, round-bottom flask was fitted a pressure-equalizing dropping funnel and a reflux condenser attached to a nitrogen inlet. In the flask were placed 1 g (0.012 mol) of cyclopentenone and 20 mL of dry methylene chloride. The flask was immersed in a dry ice−acetone bath. Titanium chloride (1.34 mL, 0.012 mol) was slowly added by a syringe to the stirring mixture. The solution turned yellow at this time. After 5 min, a solution of 1.64 g (0.012 × 2 mol) of allyltrimethylsilane in 20 mL of dry methylene chloride was added dropwise with stirring over a 10-min period. The resulting red-violet reaction mixture was stirred for 2 h at −78 °C. Then, it was hydrolyzed by addition of 25 mL of water and, after the addition of 30 mL of ethyl ether with stirring, allowed to warm to room temperature. The organic layer and the ether extracts were combined and washed successively with 30 mL of saturated $NaHCO_3$ and 30 mL of brine, dried over Na_2SO_4, and evaporated at reduced pressure. Bulb-to-bulb distillation using a Kugelrohr apparatus led to the volatile allylcyclopentanone in >97% purity.[33] ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.76 (m, 1H), 5.03 (d, J = 19 Hz, 1H), 5.02 (d, J = 10 Hz, 1H), 2.0−2.4 (m, 7H), 1.8 (m, 1H), 1.6 (m, 1H).

Synthesis of the Triflate.[34] A solution of 3-allylcyclopentanone (1 g) in 10 mL of dimethoxyethane was added to a solution of LDA (1.1 equiv, 1.5 M, 5.9 mL) in 5 mL of DME at −78 °C. The resultant solution was allowed to stir for 2 h. A solution of *N*-phenyltrifluoromethanesulfonimide (1.07 equiv, 3.08 g) in 10 mL of DME was then added and the reaction mixture was stirred at 0 °C for 9 h. After removal of solvent on the rotary evaporator, the resulting yellow oil was purified by chromatography on silica gel (hexane elution) to yield the enol triflate product. The two regio-isomers were separated by preparative GC. The regio-isomer carried forward gave ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.71 (m, 1H), 5.55 (m, 1H), 5.04 (d, J = 18 Hz, 1H), 5.02 (d, J = 10 Hz, 1H), 2.0−2.8 (m, 7H).

Organocopper Coupling to Generate 10.[35] A solution of magnesium vinylcuprate was prepared by adding 3.83 mL (1 M, 3.83 mmol) of vinylmagnesium bromide in THF to a stirred slurry of CuI (0.507 g, 2.663 mmol) in 5 mL of THF at 0 °C. 1-Trifluoromethanesulfonyloxy-4-allylcyclopent-1-ene (0.2 g, 0.78 mmol) in 5 mL of THF was added, and the reaction mixture was stirred at −15 °C (ethylene glycol−dry ice bath) for 15 h. The reaction mixture was then diluted with hexanes, filtered through a pad of Florisil, and concentrated on the rotary evaporator. Pure **10** was obtained by preparative GC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.54 (m, 1H), 5.78 (m, 1H), 5.66 (m, 1H), 4.95−5.10 (m, 4H), 2.0−2.8 (m, 6H), 1.58 (m, 1H). ^{13}C NMR (75 MHz,

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$CDCl_3$) δ 142.4, 137.4, 134.4, 129.7, 115.1, 113.3, 40.4, 38.5, 36.5, 29.9. MS, *m/e* (rel intensity) 134 (20), 105 (17), 93 (100), 91 (90), 77 (75), 65 (20). HRMS cacld for $C_{10}H_{14}$ (M^+) 134.1095, found 134.1092.

General Procedure for the Pyrolysis of Diiodides through the MeLi Hot Tube. Oven-dried Pyrex tubes (3 mm i.d., 1−1.5 cm in length) were put in a 100-mL round-bottom flask under argon. A solution of methyllithium (1.4 M in ethyl ether, 25 mL) was injected into this flask with a syringe. The ethyl ether was carried off by an argon flow. In this way, methyllithium was coated on the glass tubes. In a glove bag, the methyllithium-coated glass tubes were transferred to the pyrolysis oven under argon. Then, the oven was quickly installed on the vacuum line. The round-bottom flask containing the vicinal-diiodide under study was purged with argon and connected to the open end of the oven right after the oven was attached. The system was then evacuated to 0.001 Torr. Liquid nitrogen was filled into the cold finger of the trap. The FVP oven was then heated externally through the control of a Variac and the diiodide was heated by an air bath to 70−80 °C. The reaction usually took ~1 h. Then, vacuum was released and the products on the cold finger were rinsed off with the appropriate solvent.

Pyrolysis of 1,2-Diiodoadamantane (11) through the MeLi Tube. About 400 mg of **11** was placed in a round-bottom flask. The general procedure for pyrolyzing iodides through a MeLi-packed hot tube was followed. The products condensed on the cold finger were rinsed off with an appropriate solvent (ether for preparative GC or $CDCl_3$ for NMR).

Pyrolysis of 1- and 2-Iodoadamantane through the MeLi Tube. The round-bottom flask containing about 200 mg of the monoiodoadamantane was purged with argon and attached to the oven packed with MeLi-coated glass tubes. The general procedure for pyrolyzing iodides through a MeLi-packed hot tube was followed. The product condensed on the cold finger was rinsed off with an appropriate solvent (ether for preparative GC or $CDCl_3$ for NMR) and analyzed by GC/MS.

Synthesis of *trans*-2,3-Diiodobicyclo[2.2.2]octane.[36] Copper(II) tetrafluoroborate (0.95 g, 4.0 mmol) was added to a mixture of methylene chloride (20 mL), sodium iodide (3.0 g, 20 mmol), and iodine (1.52 g, 6 mmol) at room temperature under argon. The mixture was stirred for 4 h. The precipitated copper(I) iodide was removed by suction filtration. Extra methylene chloride was used to rinse the solid. The combined methylene chloride layers were washed with 30-mL portions of 10% sodium thiosulfate, 10% sodium bicarbonate solutions, and water, successively. $CaSO_4$ was used to dry the solution. Rotary evaporation removed the solvent and gave product in >85% purity. The pure product was obtained by running the crude material though a silica gel column using hexanes as eluent. ^1H NMR (300MHz, $CDCl_3$) δ 4.63 (s, 2H), 1.6−2.1 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) 42.7, 36.0, 25.6, 21.2. MS, *m/e* (rel intensity) 128 (44), 167 (15), 181 (10), 235 (100), 362 (2). HRMS calcd for $C_8H_{12}I_2$ (M^+) 361.9032, found 361.9028.

Pyrolysis of *trans*-2,3-Diiodobicyclo[2.2.2]octane through the MeLi Tube. The diiodide (400 mg) was placed in a round-bottom flask and purged with argon. After MeLi-coated tubes were put in the oven, the flask containing diiodide was attached right away, and the general pyrolysis procedure was followed.

Synthesis of Compound 13. Compound **13** was synthesized by the procedure of Neuman and Holmes.[37] ^1H NMR (300 MHz, $CDCl_3$) δ 5.4 (s, 1H), 2.2 (br, 2H), 0.9−2.0 (m, 11H). MS, *m/e* (rel intensity) 79 (37), 91 (66), 105 (25), 133 (56), 175 (5), 261 (100), 388 (4). HRMS calcd for $C_{10}H_{14}I_2$ (M^+) 387.9189, found 387.9190.

Pyrolysis of 13 through the MeLi Tube. **13** (300 mg) was used and the general procedure for pyrolyzing diiodides was followed.

Pyrolysis of 11 in the MeLi Tube in the Presence of 1,3-Butadiene. The general procedure for pyrolyzing diiodides through a MeLi tube was followed except for one small change in the apparatus. Butadiene was condensed in a tube fitted with a T-shape joint with the Teflon needle valve closed. One end of the T-joint was attached to the MeLi-packed oven. Compound **11** was placed in the joint between the needle valve and the oven. After the oven was heated to 100 °C, the diiodide was sublimed with a heat gun. The needle valve was open at the same time to let in the butadiene. During the course of the reaction, butadiene was cooled in an ice bath. The major product, compound **12**, has been described in the literature.[17]

Compound 14: ^1H NMR (270 MHz, C_6D_6) δ 5.87 (m, 1H), 5.04 (d, $J = 10$ Hz, 1H), 5.02 (d, $J = 20$ Hz, 1H), 0.8−2.5 (m, 17H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 114.0, 44.3, 39.9, 39.5, 38.1, 34.0, 31.7, 30.1, 29.4, 27.7, 25.4, 23.1, 13.8. MS, *m/e* (rel intensity) 55 (42), 69 (40), 79 (100), 91 (81), 105 (29), 131 (88), 173 (27), 188 (19). HRMS calcd for $C_{14}H_{20}$ (M^+) 188.1566, found 188.1559.

Dehalogenation of 13 with BuLi in the Presence of Butadiene. The procedure described in the literature[17] for 1,2-diiodoadamantane (**11**) in the presence of butadiene was followed.

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