was added to precipitate LTc as a flocculent off-white solid. The LTc was collected by vacuum filtration through a 13-mm Nylon 66 0.45-μm membrane (Alltech) with air drawn through the precipitate to dry it. The sample was then placed under vacuum (<1 mmHg) overnight. This procedure afforded yields of up to 50% for runs in acetonitrile (with acetic acid) and up to 70% yields for runs in phosphate buffer.

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Registry No. Tc, 60-54-8; Tc·HCl, 64-75-5; LTc, 115747-16-5.

Intramolecular [4 + 2]-Cycloaddition Chemistry of Some 1,3-Dienyl-Substituted Cyclopropenes

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The thermal reaction of several 1,3-dienyl-substituted diphenylcyclopropenes has been studied. Thermolysis of these systems give products derived from an intramolecular [4 + 2]-cycloaddition. The reaction involves bond formation between the dienyl π-bond and the cyclopropene to produce a diradical intermediate which collapses to the observed product. In addition to the [4 + 2]-cycloadduct, another compound formed corresponds to the [2 + 2]-adduct. During the course of our studies with (triphenylcyclopropenyl)cyclopentadiene, we found that variously substituted cyclopropenes react with 4-phenyl-1,2,4-triazoline-3,5-dione to give rearranged urazole derivatives. The reaction involves electrophilic addition of PTAD on the reactive π-bond to give an aziridinium ion which undergoes facile rearrangement followed by dipole collapse to produce the urazole. The bimolecular Diels–Alder reaction of 1-phenyl-2-vinyl-3,3-dimethylcyclopropene with *N*-methyl-1,2,4-triazoline-3,5-dione was also examined and was found to afford a novel rearranged cycloadduct.

The chemistry of cyclopropene derivatives has attracted considerable interest mainly because of the high strain energy in the ground state associated with the unsaturated three-membered ring.[1-10] One of the ways of relieving bond angle strain in cyclopropenes involves [4 + 2]-cycloaddition across the reactive π-bond.[11] With the notable exception[12,13] of molecules containing bulky groups at C_3, cyclopropenes readily undergo Diels–Alder cycloaddition to give bicyclo[4.1.0]hept-3-enes in good yield.[14] The bimolecular [4 + 2]-reaction of substituted cyclopropenes is usually subject to a strong steric preference for an exo transition state leading to the Diels–Alder cycloadduct.[3,15] The preference for exo approach is the result of an unfavorable steric interaction of the geminal substituents in the 3-position with the diene in the endo transition state. Only in instances in which the endo

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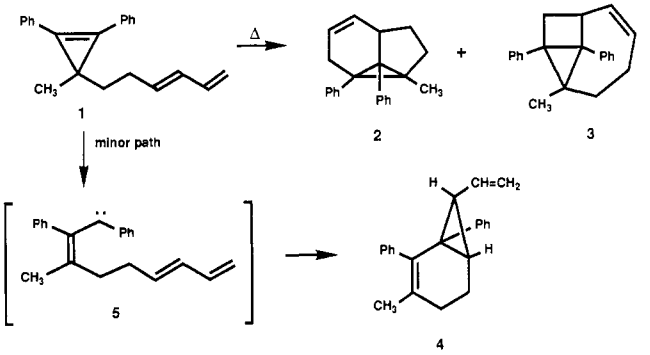
transition state is comparable with or less sterically demanding than the exo transition state have products derived from endo approach been observed.[15] In such instances the [4 + 2]-cycloaddition proceeds at reduced rates and requires the use of pressure promoted Diels–Alder conditions for observable reaction.[16]

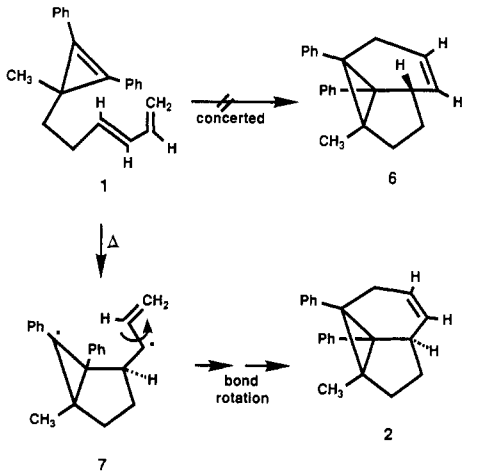
Despite prolonged interest in the [4 + 2]-cycloaddition chemistry of cyclopropenes[1-4] intramolecular examples have received surprisingly little attention.[17,18] During the past decade, there has been intense interest in the development of intramolecular cycloaddition processes.[19,20] Diels–Alder reactions,[21-23] dipolar cycloadditions,[24-28] and photochemical cyclobutane formation,[29,30] when performed intramolecularly, often display exceptional regio- and stereochemical control. In our previous studies dealing with cyclopropenes, we have found that these compounds readily undergo cycloaddition chemistry via diradical intermediates producing novel polycyclic ring systems.[31] In order to further evaluate the cycloaddition behavior of these strained rings, we decided to study the intramolecular Diels–Alder reaction of several dienyl substituted cyclopropenes. The results of this investigation are described herein.

Results and Discussion

Internal cycloadditions have been found to offer a powerful solution to many problems in complex natural product synthesis.[19,20] Converting olefin geometry into the stereochemistry of saturated carbon combined with forming two rings simultaneously from acyclic precursors accounts for the popularity of this approach. Earlier work in our laboratory has established that cyclopropene derivatives containing π-unsaturation at the 2- or 3-position of the ring can undergo intramolecular [2 + 2]-cycloadditions.[31,32] The driving force for the reaction is undoubtedly associated with the considerable relief of bond angle strain of the cyclopropene ring. As a continuation of our investigations in this area, we were particularly interested in determining whether an intramolecular Diels–Alder reaction would also occur with a 2- or 3-dienyl-substituted side chain. As our first model we chose to investigate the thermal behavior of 6-(2,3-diphenyl-1-methylcyclopropen-1-yl)-1,3-hexadiene (1). This compound was prepared by treating diphenylmethylcyclopropenyl perchlorate with the Grignard reagent derived from 1-bromo-3,5-hexadiene.[33] Heating cyclopropene 1 at 100 °C gave rise to a mixture of three isomeric products whose structures were assigned as compounds 2–4 on the basis of their spectral properties (see the Experimental Section).



Isolation of the bicyclo[4.1.0]heptene system as the minor product (i.e. 4, 12%) can nicely be rationalized in terms of opening of the cyclopropene ring to a vinylcarbene intermediate (5), which undergoes a subsequent addition of the carbene carbon onto the neighboring double bond.[34] The major component of the reaction mixture (2, 48%) formally corresponds to the intramolecular Diels–Alder cycloadduct. A concerted cycloaddition reaction from the *E*-diene 1 would be most unlikely since it would necessitate formation of the highly strained bicyclic isomer 6, which in fact, is not observed. Rather the results can be most simply interpreted on the basis of stepwise bond formation between the 3-dienyl π-bond and the cyclopropene ring to produce a diradical intermediate (7), which collapses to the observed cycloadduct after rotation about the σ-bond.



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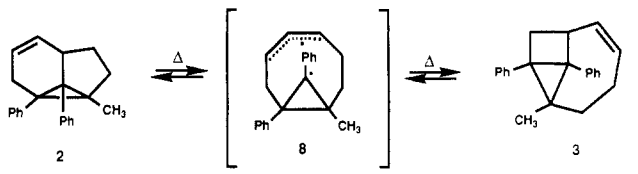
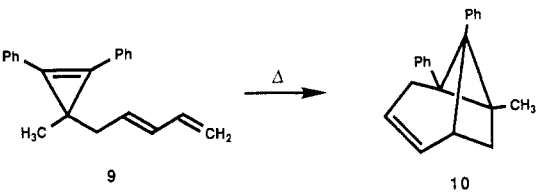
The formation of the third product (**3**, 22%), which corresponds to an intramolecular [2 + 2]-cycloadduct, derserves some comment. We had previously reported that the thermolysis of 3-alkenyl-substituted cyclopropenes can result in an intramolecular [2 + 2]-cycloaddition reaction.[54] Generally, the thermal [2 + 2]-cycloaddition of untwisted ethylenes to form cyclobutanes is a rare phenomenon.[38-43] The constraints imposed upon such reactions by orbital symmetry factors make them of more than usual mechanistic interest.[44] In cyclopropene, the torsional angle is close to zero and p-p overlap should not be significantly different from that of a normal olefin. Thus, the likelihood of cyclopropene to under [2 + 2]-cycloaddition should primarily be due to relief of angle bending rather than torsional strain. The intramolecular [2 + 2]-cycloaddition encountered on thermolysis of the diphenylmethylcyclopropene system **1** is unique in that the reported examples of thermal olefin cycloadditions generally occur in compounds in which the double bond is subjected to severe torsional strain[45-50] or else involve reactants that bear substituents capable of stabilizing diradical or dipolar intermediates.[51-53] As was pointed out in earlier papers,[54] the thermal [2 + 2]-cycloaddition reaction of 3-alkenyl-substituted cyclopropenes involves π-π bridging so as to generate the most stable diradical intermediate. The formation of cycloadduct **3**, however, involves a more complicated mechanism since there does not seem to be a route by which diradical **7** can directly produce **3**. A clue to its origin was gleaned by the finding that the thermolysis of the Diels–Alder adduct **2** gave **3** in modest yield.[55] Thus, the formation of **3** may be pictured as proceeding by a 1,3-sigmatropic rearrangement of the initially formed Diels–Alder product **2**. Subsequent studies also showed that **3** is not a primary reaction product and is only formed on prolonged heating of **2**.[55]

As an extension of our studies in this area we have also examined the thermal behavior of the next lower homologue so as to determine what effect a variation in the spatial proximity would have on the course of the reaction. Heating a sample of cyclopropene **9** at 180 °C for 72 h gave



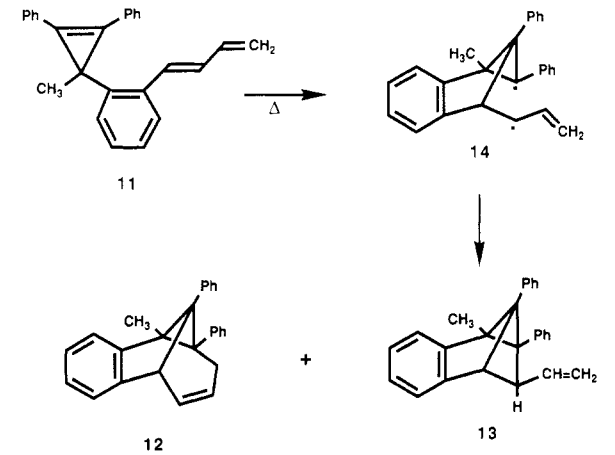
2 8 3

tricyclooctene **10** in 52% isolated yield. The formation of **10** formally corresponds to a Diels–Alder cycloaddition and presumably occurs in a stepwise manner analogues to that described with the higher homologue **1**.[56]



9 10

Additional examples which would provide further support for the generality of the stepwise intramolecular Diels–Alder reaction of dienyl-substituted cyclopropenes were sought. With this in mind, we investigated the thermal chemistry of 1-[2-(1-methyl-2,3-diphenylcyclopropen-1-yl)phenyl]buta-1,3-diene (**11**). Upon being heated at 110 °C for 6 h, **11** was converted into a 2:1 mixture of 8-methyl-1,9-diphenyl-6,7-benzotricyclo[4.3.3.0^{1,8}]non-3-ene (**12**) (42%) and 2-vinyl-6-methyl-1,7-diphenyl-4,5-benzotricyclo[3.2.0.0^{1,6}]heptane (**13**) (21%). This reaction can also be envisaged as proceeding by attack of the dienyl double bond onto the cyclopropene ring to give diradical intermediate (**14**) which collapses to either the [2 + 2]- or [4 + 2]-cycloadducts (**13** and **12**, respectively).



11 14 12 13

The intramolecular Diels–Alder reaction of furans is known to provide a means of constructing highly functionalized carbobicycles.[57] An unfavorable equilibrium toward starting material must be alleviated in systems

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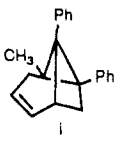
(55) Heating a sample of **2** produced **3** (30% yield) together with recovered starting material thereby suggesting an equilibration of both products under the thermal conditions employed. The possibility also, exists that diradical intermediate **8** is directly involved in the cycloaddition of **1** to **2**. However, this would require a prior isomerization about the trans double bond in cyclopropene **1**. It should be noted that all attempts to detect the *cis*-vinyl-substituted alkene in the reaction mixture failed. Compound **4** was shown to be stable to the thermal conditions used and no isomerization of the *exo*-vinyl group to the endo isomer was detected.

(56) It should be pointed out that the reaction of **9** could also occur by initial isomerization about the *E* double bond followed by a [2 + 2]-cycloaddition across the terminal π-bond. This would result in the formation of cycloadduct **i** whose NMR properties would be very similar to structure **10**. NOE experiments are more consistent with **10** as the structure of the cycloadduct.



i

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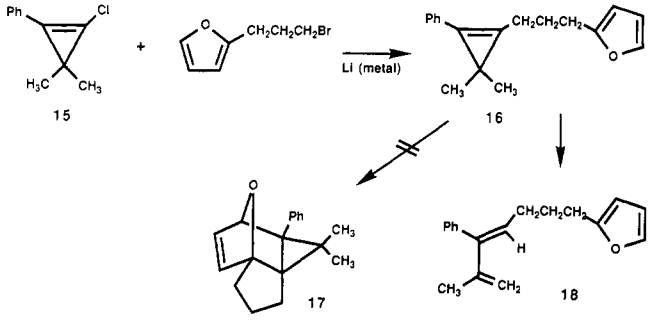
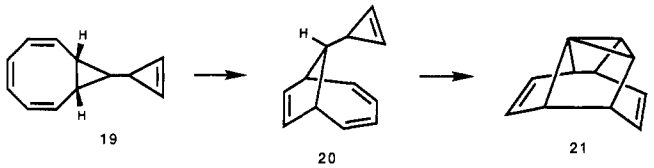
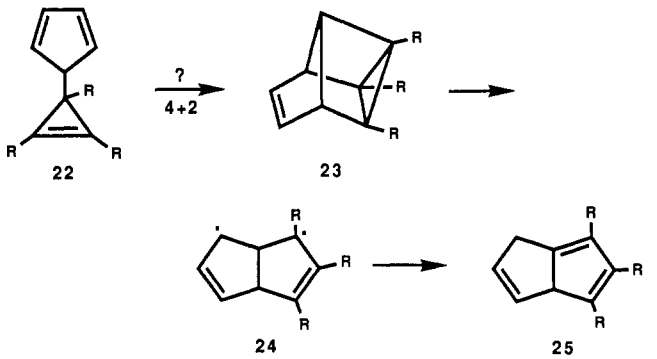
which incorporate a furan diene connected to a dienophile by three, four, or five carbon atoms. To date, methods employed to alter the equilibrium ratio have involved the use of heat,[58] cyclodextrin,[59] aqueous solutions,[60] substituted side chains,[61] and high pressure (14 kbar),[62] with the most successful of these being the use of substituted side chains and activated dienophiles. Since we are interested in the intramolecular [4 + 2]-cycloaddition reactions of cyclopropene derivatives, we undertook a study of the thermal chemistry of 2-[3-(3,3-dimethyl-2-phenyl-1-cyclopropen-1-yl)prop-1-yl]furan (**16**). As a consequence of the high strain energy associated with the cyclopropene ring, the cycloreversion reaction should not be a problem with this system. The furanyl-substituted cyclopropene **16** was prepared via the sequence of reactions outlined below. Treatment of 1-phenyl-2-chloro-3,3-dimethylcyclopropene (**15**)[63] with lithium metal followed by reaction with 2-(3-bromopropyl)furan gave the desired furan in 78% yield. Unfortunately, thermolysis of **16** failed to provide the intramolecular [4 + 2]-cycloadduct **17**. Instead, the only identifiable product (50%) corresponded to furanylheptadiene **18** derived by cleavage of the cyclopropene ring. The failure to cycloadd intramolecularly with this system is presumably a consequence of the limited dienophilic reactivity of the furan ring.



There are several other reports in the literature indicating that cyclopropenes can act as dienophiles in intramolecular Diels–Alder reactions.[64] A particularly interesting example was uncovered by Farnum and co-workers which involved the conversion of the cyclopropenyl-substituted cyclooctatriene **19** to pentacyclododecadiene **21** via the intramolecular Diels–Alder reaction of an intermediate bicyclo[4.2.1]nonatriene **20**.[64]



In our systematic pursuit of synthetic applications of the intramolecular Diels–Alder reaction of bicyclic systems containing a cyclopropene ring, we thought it would be of interest to examine the thermal behavior of a cyclopropenyl-substituted cyclopentadiene (i.e. **22**). 5-Substituted cyclopentadienes can react efficiently to form 7-substituted norbornenes, but only if the temperature is kept low enough to prevent 1,5-H shifts from preceding the Diels–Alder reaction.[65] With intramolecular Diels–Alder reactions, the conditions are usually drastic enough to allow 1,5-H shifts to precede cycloaddition, but the products of cycloaddition are normally dependent only on the chain length separating diene and dienophile, and not on the initial cyclopentadiene isomer. If the chain length is two atoms the product is exclusively the 2,7-bridged norbornene, and if the chain length is >2 atoms, the product is exclusively the 1,2-bridged isomer.[65] Internal [4 + 2]-cycloaddition of **22** might give rise to tetracyclooctene **23**, which, in the parent system, is known to produce a set of equilibrating dihydropentalenes upon thermolysis.[66] Cyclopentadiene has been used extensively for the formation of bicyclo[2.2.1]heptane compounds and as precursors to natural products.[23] The occurrence of several naturally occurring bridging sesquiterpenes has recently led to the development and effective use of the intramolecular cycloaddition reaction of substituted cyclopentadienes.[67]



Our approach to the synthesis of cyclopropene **22** (R = Ph) involved the reaction of cyclopentadienyl thallium with triphenylcyclopropenyl perchlorate.[68] Monosubstituted cyclopentadienes are usually obtained as a mixture of isomers due to rapid thermal or base-induced isomerizations of the initially formed 5-substituted isomer to the more stable 1- and 2-substituted isomers unless special precautions are taken.[69] However, we observed repeatedly that cyclopentadienylthallium and the perchlorate salt gave one single crystalline isomer which was isolated by column chromatography. The NMR spectrum showed, apart from the vinylic and aromatic protons, a two proton doublet at 2.97 ppm which is compatible with cyclopentadiene **26**. We assume that cyclopentadiene **26** is formed by a rapid [1,5]-sigmatropic hydrogen shift of the initially produced 5-substituted isomer **22**. Attempts to

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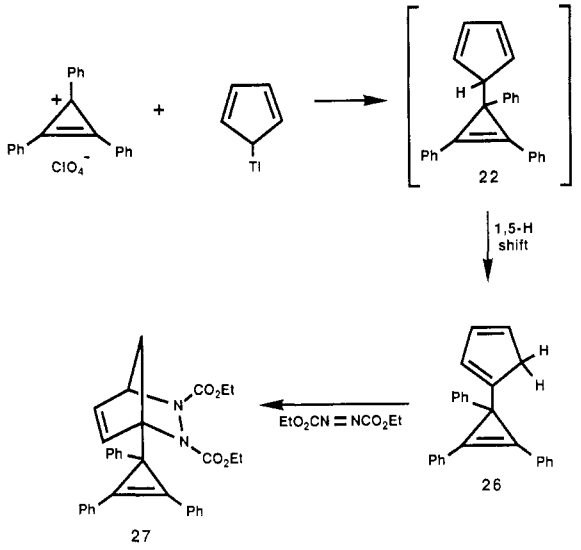
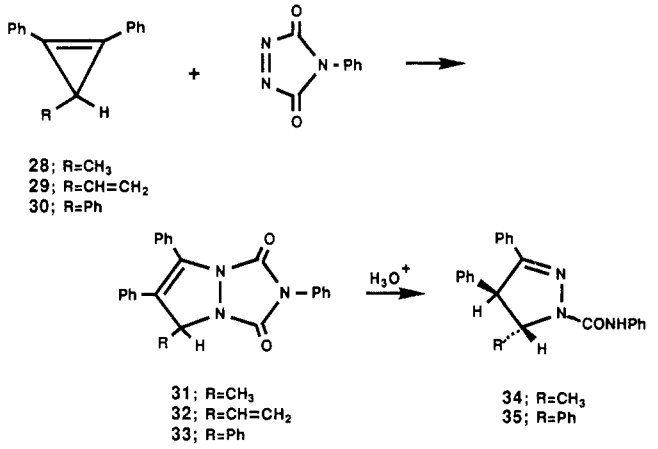
trap the 5-substituted isomer with diethyl azodicarboxylate only afforded the Diels–Alder adduct **27** derived from **26**. Unfortunately, no intramolecular cycloaddition occurred even at elevated temperatures.

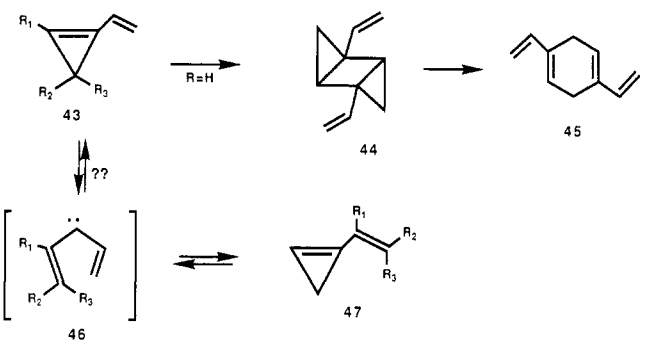


During the course of our trapping studies with diethyl azodicarboxylate (DEAD), we found that a 2:1 adduct was also formed, especially if an excess of the trapping agent was used. Since we suspected that a reaction occurred between DEAD and the cyclopropene portion of the product, we decided to probe the chemistry involved here using simpler systems. Toward this end, we treated several diphenyl-substituted cyclopropenes (**28–30**) with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) and found that a smooth reaction occurred in all cases giving rise to urazole derivatives **31–33**. These materials are readily hydrolyzed to *N*-benzamido-4,5-dihydro-1*H*-pyrazoles (i.e. **34** and **35**).

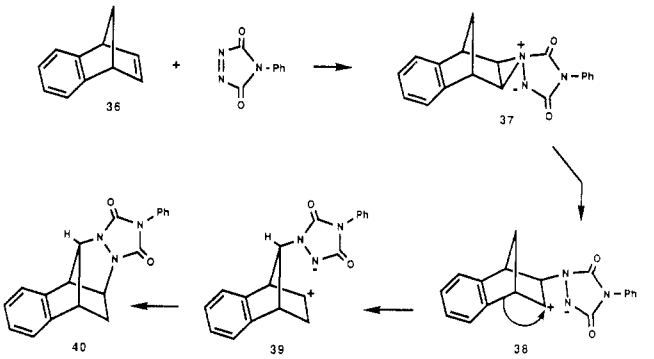


The formation of urazoles from the reaction of 4-phenyl-1,2,4-triazoline-3,5-dione with strain π-bonds has been extensively investigated by Adam and co-workers.[70] One of the early examples of this cycloaddition involves the formation of the rearranged urazole **40** from the reaction of benzonorbornadiene with PTAD. The mechanism proposed involves electrophilic addition of PTAD on the reactive π-bond, giving rise to an aziridinium ion intermediate **37**. This transient species undergoes ring

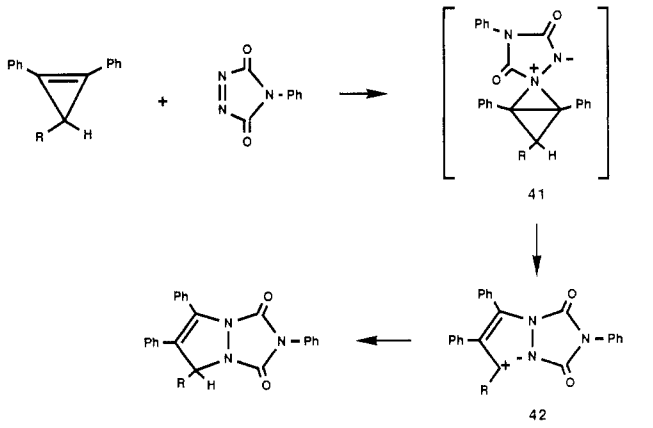
Scheme I



opening to the 1,4-dipole **38** and a subsequent Wagner–Meerwein rearrangement and collapse of the resulting 1,5-dipole **39** gives the rearranged urazole **40**.



We believe that a related mechanism is involved in the reaction of cyclopropenes with PTAD. Thus, we propose that PTAD behaves as a very speecific electrophilic reagent that attacks the cyclopropene ring to give an aziridinium ion **41**. This is followed by a rapid ring opening to produce the allyl stabilized 1,5-dipole **42**, which collapses to the observed urazole derivative.

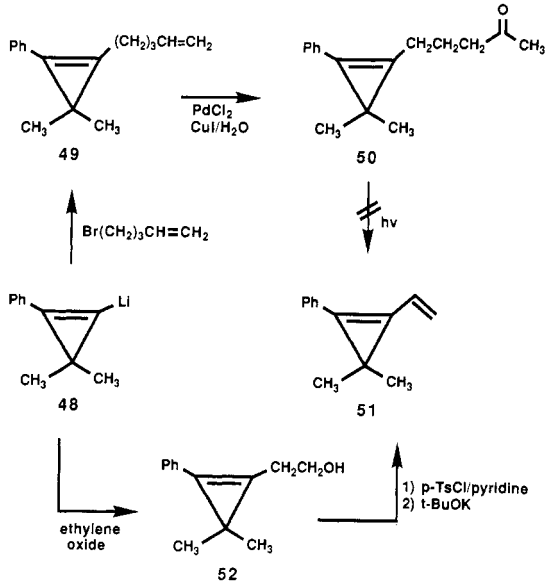


The developments up until now have focused primarily on using the highly strained cyclopropene π-bond as the dienophile in Diels–Alder reactions. In our view, vinylcyclopropenes of type **43** should also prove to be interesting molecules whose [4 + 2]-cycloaddition behavior would be worthy of study. Although the parent system is known,[71] it rapidly undergoes dimerization at temperatures greater than −100 °C. The dimerization of **43** to **44** is exothermic by 39 kcal and this would account for the facility with which the reaction occurs for the parent system.[71] Vinylcyclopropene **43** is also of some interest with regard to its conversion into divinyl carbene **46**. This process could lead to the degenerate rearrangement illustrated in Scheme

(70) Adam, W.; DeLucchi, O. *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 762. Adam, W.; DeLucchi, O.; Erden, I. *J. Am. Chem. Soc.* **1980**, *102*, 4806. Adam, W.; DeLucchi, O. *Tetrahedron Lett.* **1981**, 929. Adam, W.; DeLucchi, O.; Hill, K. *J. Am. Chem. Soc.* **1982**, *104*, 2934; *Chem. Ber.* **1982**, *115*, 1982. Adam, W.; Carballeira, N. *J. Am. Chem. Soc.* **1984**, *106*, 2874.

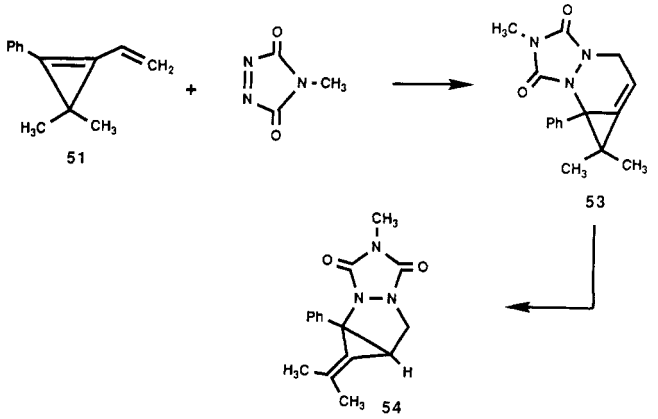
(71) Billups, W. E.; Lin, L. J. *Tetrahedron* **1986**, *42*, 1575.

I (R = H). Accordingly, we set out to develop a synthesis of 1-phenyl-2-vinyl-3,3-dimethylcyclopropene (**51**) which we believed would be stable enough to isolate and would be unlikely to undergo the [2 + 2]-dimerization reaction. Phenylcyclopropenes where both 3-positions are substituted with alkyl groups do not dimerize.[72] One approach to the desired cyclopropene would involve a Norrish type II reaction of cyclopropenyl ketone **50**.[73] Preparation of



the requisite ketone was realized by direct application of the general procedure developed by Tsuji.[74] Unfortunately, we have not found the Norrish type II reaction to be a satisfactory method for the formation of cyclopropene **51**. An alternate route which works quite well involves treating the lithiate **48** derived from 1-chloro-2-phenyl-3,3-dimethylcyclopropene[63] with ethylene oxide to give alcohol **52**. Base-induced elimination of the corresponding tosylate gave **51** in 73% yield.

With this material on hand, we investigated its reaction with *N*-methyl-1,2,4-triazoline-3,5-dione. Cycloaddition occurred readily at 0 °C, and chromatographic workup resulted in the isolation of cycloadduct **54** as the major reaction product in 46% yield. The formation of **54** can be rationalized in terms of an initial Diels–Alder reaction to give **53** which rearranges to the thermodynamically more stable isomer **54** by means of a 1,3-sigmatorpic shift.[75]



(72) DeBoer, C. D.; Wadsworth, D. H.; Perkins, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 861.
(73) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.
(74) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 145.
(75) More than likely the conversion of **53** to **54** proceeds via a trimethylenemethane diradical intermediate.

In conclusion, the results obtained from this investigation indicate that cyclopropenes possessing 1,3-dienyl side chains undergo a novel intramolecular [4 + 2]-cycloaddition via a stepwise mechanism involving a diradical intermediate. The subtle variation of behavior as a function of the nature of the side chain attached to the cyclopropene ring continues to provide mechanistic challenge. Further studies dealing with the Diels–Alder chemistry of 1-phenyl-2-vinyl-3,3-dimethylcyclopropene are in progress and will be reported in due course.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on a Varian EM-390, a Nicolet 360, and a GE QE-300 MHz spectrometer. ^{13}C NMR spectra were recorded on an GE QE-300 (75 MHz) spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a VG MM-7070S mass spectrometer at an ionizing voltage of 70 eV.

Preparation and Thermolysis of 6-(2,3-Diphenyl-1-methylcyclopropen-1-yl)-1,3-hexadiene (1). A solution containing 1.88 g of 1-bromo-3,5-hexadiene[33] in 40 mL of dry ether was added to a mixture containing 1.13 g of resublimed magnesium chips and 10 mL of dry ether over a period of 5 h. The reaction was initiated by the addition of a catalytic amount of 1,2-dibromomethane. The mixture was heated at reflux for 20 min, cooled to 0 °C, and then added to slurry containing 3.53 g of 3-methyl-1,2-diphenylcyclopropenyl perchlorate[76] in 20 mL of dry ether at −78 °C. The reaction mixture was allowed to warm to room temperature over a period of 10 h and was quenched with a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether layers were dried over magnesium sulfate and concentrated under reduced pressure to give a dark brown oil. This material was purified by silica gel chromatography using hexane as the eluent to give 1.14 g (34%) of 6-(2,3-diphenyl-1-methylcyclopropen-1-yl)-1,3-hexadiene (**1**): NMR ($CDCl_3$, 60 MHz) δ 1.47 (s, 3 H), 2.02 (d, 4 H, J = 1.5 Hz), 4.7–6.4 (m, 5 H), and 7.18–7.80 (m, 10 H); IR (neat) 1800, 1650, 1493, 1450, 1370, 1065, 995, 945, 889, 752, and 680 cm^{-1}; UV (95% ethanol) 228 (ϵ 24 000), 312 (ϵ 16 500), 319 (ϵ 18 000), and 337 nm (ϵ 11 300). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.13; H, 7.58.

A solution containing 295 mg of **1** in 5 mL of a 4:1 benzene–pyridine mixture was heated in a sealed tube at 100 °C for 54 h. The solvent was removed under reduced pressure, and the residue was chromatographed on a 1 × 5 cm silica gel column using hexane as the eluent to give 368 mg of a clear oil. This material was subjected to medium-pressure silica gel chromatography using a 10% silver nitrate impregnated column with a 1:1 ether–hexane mixture as the eluent. The major fraction was rechromatographed on a reverse HPLC column using acetonitrile–water as the eluent. The first fraction contained 64 mg (22%) of a colorless oil whose structure was assigned as 1,9-diphenyl-2-methyltricyclo-[5.2.0.0^{2,9}]non-5-ene (**3**) on the basis of its spectral properties: NMR (CCl_4, 360 MHz) δ 0.92 (s, 3 H), 1.75–1.86 (m, 1 H), 1.96–2.13 (m, 3 H), 2.18–2.26 (m, 1 H), 2.49 (ddd, 1 H, J = 18.5, 6.2, and 3.5 Hz), 3.02 (ddd, 1 H, J = 8.4, 4.5, and 2.0 Hz), 5.49 (ddd, 1 H, J = 10.7, 4.0, and 3.5 Hz), 6.12 (ddt, 1 H, J = 10.7, 8.4, and 2.0 Hz), and 6.80–7.18 (m, 10 H); IR (CCl_4) 3090, 2820, 1605, 1540, 1490, 1454, 1380, 1265, 1080, and 1005 cm^{-1}; UV (95% ethanol) 260 nm (ϵ 2800); m/e 286 (M^+), 257, 215, 205, 189, 178, 165, 127, 115, and 91. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.08; H, 7.65.

The second fraction isolated from the column contained 138 mg (48%) of a white crystalline solid, mp 84–85 °C, whose structure was assigned as 2,2a,2b,3,5a,5b-hexahydro-2a-methyl-2b,5b-diphenyl-1*H*-cycloprop[*cd*]indene (**2**) on the basis of its spectral data: IR (KBr) 3125, 2940, 1600, 1495, 1450, 1390, 1070, 910, 730, and 680 cm^{-1}; NMR (CCl_4, 360 MHz) δ 1.35 (s, 3 H), 1.40 (dd, 1 H, J = 11.3 and 5.7 Hz), 1.75 (dd, 1 H, J = 11.3 and

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8.3 Hz), 1.82 (td, 1 H, J = 11.3 and 5.7 Hz), 2.28 (tt, 1 H, J = 11.3 and 8.3 Hz), 2.47 (ddd, 1 H, J = 19.4, 4.7, and 1.7 Hz), 2.62 (dt, 1 H, J = 19.4 and 2.2 Hz), 2.90 (dd, 1 H, J = 8.3 and 4.7 Hz), 5.76 (ddd, 1 H, J = 10.2, 4.7, and 2.2 Hz), 5.92 (dddd, 1 H, J = 10.2, 4.7, 2.2, and 1.7 Hz), and 6.80–7.35 (m, 10 H); UV (95% ethanol) 221 nm (ϵ 12000); m/e 286 (M^+), 270, 257, 244, 214, 164, and 115. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.13; H, 7.59.

The third fraction isolated from the column contained 36 mg (12%) of a colorless oil whose structure was assigned as 1,2-diphenyl-3-methyl-7-vinyl-2-norcarene (**4**) on the basis of its spectral properties: IR (CCl_4) 3090, 2850, 1550, 1495, 1445, 1255, 1220, 1005, 985, and 910 cm^{-1}; NMR (CCl_4, 360 MHz) δ 0.05 (m, 2 H), 0.29 (t, 2 H, J = 4.0 Hz), 0.62 (m, 1 H), 1.52 (s, 3 H), 1.73 (t, 1 H, J = 8.7 Hz), 4.98 (dd, 1 H, J = 9.9 and 2.0 Hz), 5.01 (dd, 1 H, J = 17.0 and 2.0 Hz), 5.91 (ddd, 1 H, J = 17.0, 9.9, and 8.7 Hz), and 7.20–7.62 (m, 10 H); UV (95% ethanol) 320 (ϵ 10500), 302 (ϵ 13800), 238 (sh, ϵ 6500), and 230 nm (ϵ 8400); m/e 286 (M^+), 271, 258, 243, 215, 179, 167, 129, 115, and 91. Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.50.

Preparation and Thermolysis of 5-(2,3-Diphenyl-1-methylcyclopropen-1-yl)-1,3-pentadiene (9). To a solution containing 2.0 g of 1,3-pentadiene in 10 mL of tetrahydrofuran at −78 °C was added 20.6 mL of a 1.46 M n-butyllithium solution in hexane. The reaction mixture was allowed to warm to room temperature over a period of 2 h. The upper layer was discarded, and the bottom layer was added to a slurry containing 3.04 g of 3-methyl-1,2-diphenylcyclopropenyl perchlorate[76] in 50 mL of tetrahydrofuran at −78 °C. The reaction mixture was allowed to warm to room temperature over a period of 2 h and was stirred overnight. The reaction was quenched with a saturated ammonium chloride solution and extracted with ether. The ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was subjected to silica gel chromatography using hexane as the eluent to give 800 mg of a clear oil. Medium-pressure chromatography of this material on a 2 × 30 cm 10% silver nitrate impregnated silica gel column gave 400 mg (18%) of a colorless oil, which was identified as 5-(2,3-diphenyl-1-methylcyclopropen-1-yl)-1,3-pentadiene (**9**) on the basis of its spectra properties: NMR (CCl_4, 360 MHz) δ 1.44 (s, 3 H), 2.54 (d, 2 H, J = 7.6 Hz), 4.88 (dd, 1 H, J = 10.2 and 1.5 Hz), 4.97 (dd, 1 H, J = 16.9 and 1.5 Hz), 5.76 (dt, 1 H, J = 15.1 and 7.6 Hz), 5.98 (dd, 1 H, J = 15.1 and 10.2 Hz), 6.22 (dt, 1 H, J = 16.9 and 10.2 Hz), and 7.20–7.60 (m, 10 H); IR (neat) 1810, 1605, 1498, 1450, 1075, 1005, 905, 775, and 690 cm^{-1}; UV (95% ethanol) 338 (ϵ 19930), 321 (ϵ 26630), 310 (ϵ 22160), 237 (ϵ 27180), and 226 nm (ϵ 35160); m/e 202, 188, 177, 164, 115, 105, 91, and 77; mass calcd for $C_{21}H_{20}$ 272.1565, found 272.1559. Anal. Calcd for $C_{21}H_{20}$: C, 92.59; H, 7.41. Found: C, 92.43; H, 7.28.

The second fraction contained 350 mg (13%) of a clear oil whose structure was assigned as 5-(1,3-diphenyl-2-methylcyclopropen-1-yl)-1,3-pentadiene on the basis of its spectral properties: NMR (CCl_4, 360 MHz) δ 2.80 (s, 3 H), 3.45 (d, 2 H, J = 7.0 Hz), 5.42 (dd, 1 H, J = 10.2 and 1.0 Hz), 5.54 (dd, 1 H, J = 17.1 and 1.0 Hz), 6.25 (dt, 1 H, J = 15.1 and 7.0 Hz), 6.58 (dd, 1 H, J = 15.1 and 10.2 Hz), 6.76 (dt, 1 H, J = 17.1 and 10.2 Hz), and 7.08–7.45 (m, 10 H); IR (neat) 1850, 1820, 1650, 1600, 1490, 1480, 1445, 1075, 1030, 1005, 950, 900, 760, 695, and 685 cm^{-1}; UV (95% ethanol) 253 nm (ϵ 25900); m/e 244, 215, 206, 205, 189, 178, 165, 152, 128, 127, 115, 103, 91, and 77. Anal. Calcd for $C_{21}H_{20}$: C, 92.59; H, 7.41. Found: C, 92.54; H, 7.37.

A solution containing 150 mg of cyclopropene **9** in 40 mL of benzene was thermolyzed in a sealed tube at 180 °C for 72 h. The solvent was removed under reduced pressure, and the residue was passed through a 2 × 15 cm silica gel column using hexane as eluent. Reverse-phase HPLC of the major fraction afforded 80 mg (52%) of a clear oil whose structure was assigned as 2-methyl-1,8-diphenyltricyclo[4.2.0.$0^{2,8}$]oct-5-ene (**10**): NMR (CCl_4, 360 MHz) δ 1.14 (s, 3 H), 1.83 (d, 1 H, J = 10.4 Hz), 2.01 (dt, 1 H, J = 18.4 and 2.6 Hz), 2.09 (dt, 1 H, J = 18.4 and 2.6 Hz), 2.11 (dd, 1 H, J = 10.4 and 5.4 Hz), 3.12 (t, 1 H, J = 5.4 Hz), 5.55 (dt, 1 H, J = 9.6 and 2.6 Hz), 6.39 (ddt, 1 H, J = 9.6, 5.4, and 2.6 Hz), and 6.90–7.10 (m, 10 H); IR (CCl_4) 1730, 1595, 1545, 1500, 1495, 1445, 1375, 1260, 1105, 1075, and 1010 cm^{-1}; UV (95% ethanol) 262 (ϵ 5510), 248 (ϵ 4970), and 220 nm (ϵ 5130); m/e 272 (M^+), 257, 232, 215, 179, 165, 129, 115, 91, and 77. Anal. Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.43; H, 7.28.

Preparation and Thermolysis of 1-[2-(1-Methyl-2,3-diphenylcyclopropen-1-yl)phenyl]butadiene (11). To a mixture containing 1.33 g of magnesium turnings and 10 mL of dry ether was added dropwise a solution containing 6.7 g of allyl bromide in 35 mL of dry ether over a period of 1 h. The mixture was heated at reflux for 2.5 h and cooled to room temperature, and then a solution containing 6.3 g of o-bromobenzaldehyde in 25 mL of dry ether was added over a period of 30 min. The mixture was stirred at room temperature overnight and was quenched using a saturated ammonium chloride solution. The ether layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate and concentrated under reduced pressure to leave behind a thick yellow oil. Purification of this material by distillation at 84 °C (0.4 mm) gave 7.0 g (91%) of 1-(2-bromophenyl)-3-buten-2-ol: NMR ($CDCl_3$, 60 MHz) δ 2.2–2.45 (m, 2 H), 2.85–2.98 (m, 1 H), 4.86–5.32 (m, 2 H), 5.5–6.35 (m, 2 H), and 7.0–7.6 (m, 4 H); IR (neat) 3420, 1625, 1575, 1540, 1430, 1380, 1250, 1190, 1010, and 740 cm^{-1}.

A solution containing 5.7 g of the above alcohol, 7.9 g of triphenyl phosphine, 4.6 g of carbon tetrachloride, and 0.5 g of hydroquinone in 50 mL of acetonitrile was heated at reflux for 15 min. To this mixture was added 12.5 g of of triethylamine, and the mixture was heated at reflux for an additional 3 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane. The hexane extracts were concentrated under reduced pressure to give 5.1 g of a 70:30 mixture of (2-bromophenyl)butadiene and 1-(2-bromophenyl)-1-chloro-3-butene. This mixture was dissolved in 150 mL of dry ether, and 5.6 g of potassium *tert*-butoxide was added. The solution was stirred at room temperature for 12 h and was then poured into 300 mL of water. The ether layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate and concentrated under reduced pressure to leave behind a pale yellow oil which was purified by distillation at 64 °C (0.35 mm) to give 4.2 g (79%) of (2-bromophenyl)butadiene: NMR ($CDCl_3$, 360 MHz) δ 5.25 (dd, 1 H, J = 10.0 and 1.0 Hz), 5.39 (dd, 1 H, J = 16.7 and 1.0 Hz), 6.57 (ddd, 1 H, J = 15.5, 10.3, and 10.0 Hz), 6.73 (dd, 1 H, J = 16.7 and 10.3 Hz), 6.92 (d, 1 H, J = 15.5 Hz), and 7.08–7.60 (m, 4 H); IR (neat) 1665, 1615, 1480, 1450, 1340, 1175, 1065, 1000, 945, 900, 851, 760, and 690 cm^{-1}.

To a slurry containing 1.02 g of anhydrous magnesium chloride in 25 mL of tetrahydrofuran was added 0.75 g of potassium in small pieces. The mixture was heated at reflux for 3.5 h, and then a solution containing 0.84 g of (2-bromophenyl)butadiene in 10 mL of tetrahydrofuran was added with stirring. The mixture was heated for an additional hour, cooled to 0 °C, and then added to a cooled slurry containing 0.305 g of 1,2-diphenyl-3-methylcyclopropenyl perchlorate[76] in 25 mL of tetrahydrofuran at −78 °C. The mixture was stirred at −78 °C for 1.5 h, at 0 °C for 30 min, and at room temperature for 2 h. The reaction was quenched with a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was washed with ether. The combined ether extracts were dried over magnesium sulfate and concentrated under reduced pressure to leave behind a thick yellow oil. This material was purified on a 2.5 × 100 cm silica gel column using hexane as the eluent to give 0.084 g (25%) of 1-[2-(1-methyl-2,3-diphenylcyclopropen-1-yl)phenyl]butadiene (**11**): NMR ($CDCl_3$, 90 MHz) δ 1.81 (s, 3 H), 5.05–5.45 (m, 2 H), 6.28–6.84 (m, 2 H), and 7.0–7.85 (m, 15 H); IR (neat) 1800, 1600, 1455, 1430, 1390, 1055, 980, 730, and 690 cm^{-1}; UV (95% ethanol) 284 (ϵ 28000), 302 (ϵ 21000), 315 (ϵ 18000), and 332 nm (ϵ 11300). Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.08; H, 6.47.

A solution containing 400 mg of **11** in 20 mL of benzene was heated at 110 °C for 6 h in a sealed tube. The solvent was removed under reduced pressure, and the residue was passed through a 2 × 15 cm alumina column using hexane as the eluent to give 335 mg of an oil which was resubjected to medium-pressure chromatography using a 2 × 30 cm 10% silver nitrate impregnated silica gel column. The column was eluted with a 5% ether–hexane mixture to give 168 mg (42%) of 8-methyl-1,9-diphenyl-6,7-bezotricyclo[4.3.0.$0^{1,8}$]non-3-ene (**12**): NMR (CCl_4, 360 MHz) δ 1.66

(ddd, 1 H, J = 16.9, 3.6, and 2.5 Hz), 1.72 (s, 3 H), 2.38 (dd, 1 H, J = 16.9 and 7.2 Hz), 4.20 (d, 1 H, J = 7.6 Hz), 6.14 (ddd, J = 7.2, 4.5, and 2.5 Hz), 6.71 (ddd, 1 H, J = 7.6, 4.5, and 3.6 Hz), and 6.92–7.48 (m, 14 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.7, 33.1, 41.6, 44.2, 48.8, 52.3, 121.8, 123.9, 125.3, 125.9, 126.1, 126.7, 127.7, 127.9, 128.3, 129.9, 132.1, 132.4, 142.6, 142.7, 145.0, and 147.1; IR (CCl_4) 3030, 2940, 1695, 1495, 1470, 1440, 1390, 1190, 1040, 700, and 667 cm^{-1}; UV (95% ethanol) 278 (ϵ 4190), 272 (ϵ 4830), and 235 nm (ϵ 10 200); m/e 334 (M^+), 319, 241, 215, 167, 115, 105, 91, and 77. Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.19; H, 6.52.

The second fraction contained 84 mg (18%) of 2-vinyl-6-methyl-1,7-diphenyl-4,5-benzotricyclo[3.2.0.0^{1,6}]heptane (**13**): NMR (CCl_4, 360 MHz) δ 1.36 (s, 3 H), 2.24 (d, 1 H, J = 9.4 Hz), 3.39 (s, 1 H), 5.02 (dd, 1 H, J = 16.6 and 1.0 Hz), 5.06 (dd, 1 H, J = 9.7 and 1.0 Hz), 6.22 (ddd, 1 H, J = 16.6, 9.7, and 9.4 Hz), and 6.95–7.55 (m, 14 H); IR (CCl_4) 2960, 2880, 1640, 1585, 1495, 1470, 1440, and 910 cm^{-1}; UV (95% ethanol) 282 (ϵ 5320), 247 (ϵ 14 500) and 220 nm (ϵ 25 800); m/e 334 (M^+), 319, 241, 215, 202, 128, 105, 91, and 77. Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.25; H, 6.39.

Preparation and Thermolysis of 2-[3-(3,3-Dimethyl-2-phenyl-1-cyclopropen-1-yl)prop-1-yl]furan (16). To a solution containing 5.0 g of furan in 100 mL of anhydrous tetrahydrofuran at −78 °C was added 49 mL of a 1.5 M n-butyllithium solution. The mixture was allowed to warm to room temperature over a period of 3 h and was stirred for an additional 18 h. After cooling to −78 °C, 18 mL of HMPA was added and the solution was treated with 9.87 g of 1,3-dibromopropane in 20 mL of anhydrous tetrahydrofuran. The solution was allowed to warm to room temperature and was stirred overnight. After being quenched with a saturated ammonium chloride solution, the mixture was extracted with ether, and the ether extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was distilled at 58 °C (3 mm) to give 3.99 g (28%) of a clear oil whose structure was assigned as 2-(3-bromopropyl)furan on the basis of its spectral properties: NMR (CCl_4, 90 MHz) δ 2.10 (pent, 2 H, J = 7.2 Hz), 2.76 (t, 2 H, J = 7.2 Hz), 3.33 (t, 2 H, J = 7.2 Hz), 5.86–5.96 (m, 1 H), 6.06–6.16 (m, 1 H), and 7.06–7.16 (m, 1 H); IR (neat) 3100, 2960–2820, 1590, 1500, 1430, 1350, 1140, 1105, 910, 800, and 730 cm^{-1}.

To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenylcyclopropene (**15**)[63] in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C, and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min at this temperature and was quenched by the addition of 1.64 g of 2-(3-bromopropyl)furan in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at 25 °C, and this was followed by the addition of a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using hexane as the eluent to give 1.70 g (78%) of a clear oil whose structure was assigned as 2-[3-(3,3-dimethyl-2-phenyl-1-cyclopropen-1-yl)prop-1-yl]furan (**16**) on the basis of its spectral properties: NMR (CCl_4, 90 MHz) δ 1.30 (s, 6 H), 2.30 (pent, 2 H, J = 7.2 Hz), 2.60 (t, 2 H, J = 7.2 Hz), 2.73 (t, 2 H, J = 7.2 Hz, 5.80–5.95 (m, 1 H), 6.06–6.20 (m, 1 H), and 7.03–7.30 (m, 6 H); IR (neat) 3060–2820, 1830, 1595, 1500, 1490, 1440, 1360, 1150, 1070, 1000, 920, 790, 760, 730, and 690 cm^{-1}; UV (95% ethanol) 267 (ϵ 10 500) and 217 nm (ϵ 17 150); m/e 252, 195 (base), 143, 91, and 77. Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.61; H, 8.04.

A solution containing 300 mg of cyclopropene **16** in 40 mL of benzene in a sealed tube was heated at 180 °C for 16 h. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography using hexane as the eluent to give 150 mg (50%) of a clear oil whose structure was assigned as (*Z*)-2-(6-methyl-5-phenyl-4,6-heptadienyl)furan (**18**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.57 (pent, 2 H, J = 7.5 Hz), 1.83 (t, 2 H, J = 7.5 Hz), 1.87 (s, 3 H), 2.43 (t, 2 H, J = 7.5 Hz), 4.32 (s, 1 H), 4.82 (s, 1 H), 5.68 (t, 1 H, J = 7.5 Hz), 5.76–5.78 (m, 1 H), 6.11–6.13 (m, 1 H), and 6.90–7.25 (m, 6 H); IR (neat) 3080–2830, 1590, 1500, 1490, 1450, 1440, 1360, 1150, 1070, 1000, 920, 890, 800, 770, 720, and 700 cm^{-1}; UV (95% ethanol) 233 (ϵ 17 600) and 222 mm (ϵ 18 700); m/e 252 (M^+), 149, 138 (base), 105.91, and 77. Anal. Calcd for $C_{18}H_{20}$: C, 85.67; H, 7.99. Found: C, 85.55; H, 8.03.

Preparation of 1-(1,2,3-Triphenylcyclopropen-1-yl)cyclopenta-1,3-diene (26). A slurry containing 2.69 g of cyclopentadienylthallium in 30 mL of dry acetonitrile was cooled to −40 °C, and 3.67 g of 1,2,3-triphenylcyclopropenyl perchlorate[68] was added in one portion. After being stirred for 15 min, the mixture was allowed to warm to 0 °C and was stirred for an additional 4 h. The mixture was filtered to remove the thallium perchlorate, and the solvent was concentrated under reduced pressure. The residue obtained was taken up in ether and washed with water. The ether layer was separated, dried, and concentrated under reduced pressure to leave behind an oil which was purified by flash chromatography on a 5 × 15 cm column using hexane as the eluent to give 1.6 g (48%) of 1-(1,2,3-triphenylcyclopropen-1-yl)cyclopenta-1,3-diene (**26**): NMR ($CDCl_3$, 60 MHz) δ 2.97 (d, 2 H, J = 17.0 Hz), 6.07–6.69 (m, 3 H), and 7.1–7.9 (m, 15 H); IR (KBr) 3030, 1818, 1600, 1488, 1440, 1075, 1030, 900, 705, and 690 cm^{-1}; UV (95% ethanol) 227 (ϵ 25 000), 302 (ϵ 20 000), 314 (ϵ 23 000), and 330 nm (ϵ 15 800). Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.78; H, 5.87.

Preparation of Diethyl 4-(1,2,3-Triphenylcyclopropen-1-yl)-5,6-diazabicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (27). A slurry containing 2.69 g of cyclopentadienylthallium in 30 mL of dry acetonitrile was cooled to −40 °C, and 3.67 g of 1,2,3-triphenylcyclopropenylium perchlorate[68] was added in one portion. A solution containing 1.75 g of diethyl azodicarboxylate in 5 mL of dry acetonitrile was added to this mixture so as to maintain the temperature at −40 °C. After being stirred for 15 min, the mixture was allowed to warm to 0 °C and was stirred at this temperature for 4 h. The mixture was then filtered to remove the thallium perchlorate, and the solvent was concentrated under reduced pressure. The residue obtained was extracted with ether and washed with water. The ether layer was separated, dried over magnesium sulfate, and concentrated under reduced pressure to give 2.0 g (40%) of diethyl 4-(1,2,3-triphenylcyclopropen-1-yl)-5,6-diazabicyclo[2.2.1]hept-2-ene-5,6-dicarboxylate (**27**) as a clear oil: NMR ($CDCl_3$, 100 MHz) δ 0.96 (t, 3 H, J = 7.0 Hz), 1.22 (t, 3 H, J = 7.0 Hz), 2.70 (br s, 2 H), 3.98 (q, 2 H, J = 7.0 Hz), 4.18 (q, 2 H, J = 7.0 Hz), 5.01 (br d, 2 H, J = 8.0 Hz), 6.18 (br s, 1 H), and 7.01–7.88 (m, 15 H); IR (neat) 3030, 1818, 1754, 1710, 1600, 1485, 1440, 1075, 1030, 890, 760, 740, and 690 cm^{-1}. Anal. Calcd for $C_{32}H_{30}N_2O_4$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.74; H, 5.81; N, 5.46.

Preparation of 5-Methyl-*N*,3,4-triphenyl-3-pyrazoline-1,2-dicarboximide (31). To a solution containing 2.06 g of 1,2-diphenyl-3-methylcyclopropene (**28**) in 25 mL of benzene was added 1.75 g of 4-phenyl-1,2,4-triazoline-3,5-dione. The mixture was stirred for 1 h, filtered, and concentrated under reduced pressure. The resulting residue was purified by chromatography on a 2.5 × 15 cm neutral alumina column using a 40% methylene chloride–benzene mixture as the eluent. The major fraction obtained was recrystallized from acetone to give 1.8 g (52%) of 5-methyl-*N*,3,4-triphenyl-3-pyrazoline-1,2-dicarboximide (**31**) as a white crystalline solid: mp 176–177 °C; NMR ($CDCl_3$, 90 MHz) δ 1.48 (d, 3 H, J = 6.0 Hz), 5.6 (q, 1 H, J = 6.0 Hz), and 7.05–7.7 (m, 15 H); IR (KBr) 1760, 1710, 1490, 1390, 1180, 1010, 760, 690, and 640 cm^{-1}; UV (95% ethanol) 225 (ϵ 21 700) and 305 nm (ϵ 12 600); m/e 367 (M^+), 247, 191, 165, 119, 109, 91, and 77. Anal. Calcd for $C_{24}H_{19}N_3O_2$: C, 75.57; H, 5.02; N, 11.02. Found: C, 75.61; H, 5.05; N, 11.00.

A mixture containing 570 mg of **31**, 170 mg of potassium hydroxide, and 25 mL of isopropyl alcohol was heated at reflux under nitrogen for 1 h, cooled to room temperature, and neutralized with a 3 N hydrochloric acid solution. The mixture was poured into 150 mL of water, and the precipitated product was filtered and recrystallized from chloroform to give 520 mg (95%) of *N*-benzamido-3,4-diphenyl-5-methyl-4,5-dihydro-1*H*-pyrazole (**34**): mp 182–183 °C; NMR ($CDCl_3$, 90 MHz) δ 1.52 (d, 3 H, J = 6.0 Hz), 4.2 (d, 1 H, J = 4.0 Hz), 4.49 (p, 1 H, J = 6.0 and 4.0 Hz), 7.0–7.8 (m, 15 H), and 8.20 (br s, 1 H); IR (KBr) 1680, 1600, 1530, 1450, 1180, 1080, 945, 785, 745, and 685 cm^{-1}; UV (95% ethanol)

238 (ε 29000), 310 nm (ε 22000); *m/e* 354 (M^+), 255, 220, 194, 193, 165, 145, 104, 91, and 77. Anal. Calcd for $C_{23}H_{21}NO$: C, 77.75; H, 5.92; N, 11.83. Found: C, 77.80; H, 5.99; N, 11.79.

Preparation of *N*,3,4-Triphenyl-5-vinyl-3-pyrazoline-1,2-dicarboximide (32). To a solution containing 545 mg of 1,2-diphenyl-3-vinylcyclopropene (**29**) in 50 mL of benzene was added 440 mg of 4-phenyl-1,2,4-triazoline-3,5-dione in small portions. After being stirred for 1 h, the mixture was filtered and concentrated under reduced pressure. The residue was purifed by chromatography on a 4 × 15 cm neutral alumina column using a 40% methylene chloride–benzene mixture as the eluent. The major fraction obtained was recrystallized from acetone to give 610 mg (61%) of *N*,3,4-triphenyl-5-vinyl-3-pyrazoline-1,2-dicarboximide (**32**): mp 223–224 °C; NMR ($CDCl_3$, 90 MHz) δ 4.48 (d, 1 H, *J* = 6.0 Hz), 5.20–6.75 (m, 3 H), and 7.1–7.6 (m, 15 H); IR (KBr) 1770, 1710, 1600, 1510, 1415, 1145, 1030, 800, 750, 690, and 645 cm^{-1}; UV (95% ethanol) 226 (ε 24000) and 305 nm (ε 11500); *m/e* 393 (M^+), 273, 236, 221, 165, 143, 128, 115, 104, 91, and 77. Anal. Calcd for $C_{25}N_{19}N_3O_2$: C, 76.32; H, 4.87; N, 10.68. Found: C, 76.29; H, 4.87; N, 10.67.

Preparation of *N*,3,4,5-Tetraphenyl-3-pyrazoline-1,2-dicarboximide (33). To a solution containing 2.68 g of 1,2,3-triphenyl-1-cyclopropene (**30**) in 250 mL of benzene was added 1.75 g of 4-phenyl-1,2,4-triazoline-3,5-dione in small portions. After being stirred for 1 h, the mixture was filtered and concentrated under reduced pressure to leave behind a yellow solid, which was purified by chromatography on a 5 × 20 cm neutral alumina column using a 40% methylene chloride–benzene mixture as the eluent. Recrystallization of the major fraction from acetone gave 3.50 g (80%) of N,3,4,5-tetraphenyl-3-pyrazoline-1,2-dicarboximide (**33**): mp 182–183 °C; NMR ($CDCl_3$, 90 MHz) δ 6.32 (s, 1 H) and 7.0–7.6 (m, 20 H); IR (KBr) 1785, 1710, 1495, 1395, 1265, 1145, 1075, 915, 835, 740, and 680 cm^{-1}; UV (95% ethanol) 225 (ε 25000) and 302 nm (ε 13000); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 68.8, 122, 152.9, 125.4, 126.6, 137.4, and 150.9; *m/e* 443 (M^+), 367, 296, 282, 247, 178, 165, 119, 105, 91, and 77. Anal. Calcd for $C_{29}H_{21}N_3O_2$: C, 78.54; H, 4.77; N, 9.48. Found: C, 78.45; H, 4.79; N, 9.46.

A mixture containing 220 mg of **33** and 84 mg of potassium hydroxide in 20 mL of isopropyl alcohol was heated at reflux under nitrogen for 1 h. The solution was allowed to cool to room temperature and was then neutralized with a 3 N hydrochloric acid solution and diluted with 100 mL of water. The solid that formed was filtered and recrystallized from chloroform to give 167 mg (80%) of *N*-benzamido-3,4,5-triphenyl-4,5-dihydro-1*H*-pyrazole (**35**) as a white crystalline solid: mp 173–174 °C; NMR ($CDCl_3$, 90 MHz) δ 4.58 (d, 1 H, *J* = 4.0 Hz), 5.42 (d, 1 H, *J* = 4.0 Hz), 7.05–7.85 (m, 20 H), and 8.30 (br s, 1 H); IR (KBr) 1670, 1595, 1525, 1440, 1315, 1225, 1135, 1040, 835, 795, and 695 cm^{-1}; UV (95% ethanol) 228 (ε 29000) and 309 nm (ε 22000); *m/e* 417 (M^+), 298, 221, 194, 178, 165, 104, 91, and 77. Anal. Calcd for $C_{28}H_{23}N_3O$: C, 80.55; H, 5.55; N, 10.07. Found: C, 80.40; H, 5.61; N, 10.04.

Preparation and Reaction of 3,3-Dimethyl-1-phenyl-2-vinylcyclopropene (51) with *N*-Methyl-1,2,4-triazoline-3,5-dione. To a suspension containing 1.0 g of a 30% lithium dispersion in 10 mL of anhydrous ether was added 1.55 g of 1-chloro-3,3-dimethyl-2-phenycyclopropene[63] in 25 mL of anhydrous ether. The mixture was stirred at room temperature for 16 h and was then cooled to −100 °C, and 3 mL of freshly distilled HMPA was added. The resulting mixture was stirred for 30 min and was quenched by the addition of 0.38 g of ethylene oxide in 5 mL of anhydrous ether. The mixture was allowed to stir for 15 h at room temperature and was then quenched with a saturated ammonium chloride solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were dried over magnesium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using a 10% ether–hexane mixture as the eluent to give 1.0 g (61%) of a clear oil whose structure was assigned as 1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)ethan-2-ol (**52**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.26 (s, 3 H), 1.80–2.10 (br s, 1 H), 2.85 (t, 2 H, *J* = 6.9 Hz), 3.85 (t, 2 H, *J* = 6.9 Hz), and 7.00–7.40 (m, 5 H); IR (neat) 2580–3140, 3080–2810, 1830, 1600, 1490, 1440, 1360, 1040, 780, 760, and 690 cm^{-1}.

To a solution containing 0.50 g of the above alcohol in 75 mL of anhydrous pyridine was added 1.0 g of *p*-toluenesulfonyl chloride, and the mixture was cooled in the freezer for 16 h. The solution was acidified with a 10% hydrochloric acid solution and extracted with ether. The ether extracts were washed with a 10% hydrochloric acid solution, a 5% sodium bicarbonate solution, and water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure to give 0.62 g (75%) of the crude tosylate: NMR (CCl_4, 90 MHz) δ 1.20 (s, 6 H), 2.30 (s, 3 H), 2.85 (t, 2 H, *J* = 6.9 Hz), 4.20 (t, 2 H, *J* = 6.9 Hz), and 7.00–7.80 (m, 9 H). This materials was used without further purification.

A solution containing 0.62 g of the above tosylate, 0.44 g of potassium *tert*-butoxide, and 0.03 g of 18-crown-6 in 10 mL of petroleum ether was heated at 60 °C for 3 h. The mixture was then poured into water, and the water layer was extracted with petroleum ether. The combined organic layer was dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The residue was chromatographed on a 2 × 15 cm silica gel column using hexane as the eluent to give 0.25 g (73%) of a clear oil whose structure was assigned as 3,3-dimethyl-1-phenyl-2-vinylcyclopropene (**51**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.55 (s, 3 H), 5.35 (dd, 1 H, *J* = 10.1 and 2.1 Hz), 5.55 (dd, 1 H, *J* = 1.71 and 2.1 Hz), 6.20 (dd, 1 H, *J* = 17.1 and 10.1 Hz), and 7.20–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.4, 24.4, 120.9, 123.2, 124.3, 127.8, 128.5, and 128.9; IR (neat) 3040–2800, 1805, 1605, 1590, 1495, 1450, 980, 915, 770, and 695 cm^{-1}; UV (95% ethanol) 319 (ε 14000), 304 (ε 17800), 238 (ε 6480), and 230 nm (ε 8240). anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.58, H, 8.30.

To a solution containing 125 mg of the above compound in 10 mL of anhydrous methylene chloride at 0 °C was added 74 mg of *N*-methyl-1,2,4-triazoline-2,5-dione. The solution was stirred for 1 h at 0 °C and was then washed with a saturated solution of ammonium chloride. The mixture was extracted with ether, and the ether extracts were dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was chromatographed on a 1 × 15 cm silica gel column using 10% ethyl acetate–hexane as the eluent to give 100 mg (46%) of a light yellow oil whose structure was assigned as 6-isopropylidene-*N*-methyl-1-phenyl-2,3-diazobicyclo[3.1.0]hexane-2,3-dicarboximide (**54**) on the basis of its spectral properties: NMR ($CDCl_3$, 360 MHz) δ 1.74 (d, 3 H, *J* = 1.9 Hz), 1.84 (d, 3 H, *J* = 1.5 Hz), 2.35–2.40 (m, 1 H), 2.93 (s, 3 H), 3.61 (dd, 1 H, *J* = 10.7 and 4.4 Hz), 3.99 (d, 1 H, *J* = 10.7 Hz), and 7.15–7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.1, 22.9, 25.3, 35.2, 46.2, 51.3, 125.8, 127.4, 128.2, 128.5, 134.8, 135.8, 155.5, and 159.8; IR (CCl_4) 3070–2850, 1785, 1720, 1450, 1395, 1270, 1050, 990, and 770 cm^{-1}; UV (95% ethanol) 224 nm (ε 12650). Anal. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.83; H, 6.05; N, 14.83. Found: C, 67.74; H, 5.96; N, 14.61.

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Registry No. **1**, 125643-15-4; **2**, 125643-16-5; **3**, 125643-17-6; **4**, 125643-18-7; **9**, 125643-20-1; **10**, 125643-21-2; **11**, 125643-22-3; **12**, 125643-23-4; **13**, 125643-24-5; **15**, 56895-72-8; **16**, 125643-26-7; **18**, 125643-27-8; **26**, 125643-28-9; **27**, 125643-29-0; **28**, 51425-87-7; **29**, 62937-82-0; **30**, 16510-49-9; **31**, 125643-30-3; **32**, 125643-31-4; **33**, 125643-32-5; **35**, 125643-33-6; **51**, 109900-84-7; **52**, 125643-37-0; **52** tosylate, 125643-34-7; **54**, 125643-38-1; (*E*)-1-bromo-3,5-hexadiene, 57261-22-0; 3-methyl-1,2-diphenylcyclopropenylium perchlorate, 72612-89-6; 1,3-pentadiene, 504-60-9; (*E*)-5-(1,3-diphenyl-2-methylcyclopropen-1-yl)-1,3-pentadiene, 125643-19-8; 1-(2-bromophenyl)-3-buten-2-ol, 125643-25-6; 1,3-dibromopropane, 109-64-8; furan, 110-00-9; 2-(3-bromopropyl)furan, 92513-83-2; 1,2,3-triphenylcyclopropenylium perchlorate, 51778-20-2; cyclopentadienylthallium, 34822-90-7; 4-phenyl-1,2,4-triazoline-3,5-dione, 4233-33-4; diethyl azodicarboxylate, 1972-28-7; 1-chloro-3,3-dimethyl-2-phenylcyclopropene, 56895-72-8; allyl bromide, 106-95-6; *o*-bromobenzaldehyde, 6630-33-7; 1-(2-bromophenyl)-1,3-butadiene, 125643-35-8; 1-(2-bromophenyl)-1-chloro-3-butene, 125643-36-9.