1834 *J. Org. Chem.* 1983, *48*, 1834–1840

Studies Dealing with the Cycloreversion Reactions of Phenyl-Substituted 2,3-Diazabicyclo[3.1.0]hex-2-enes

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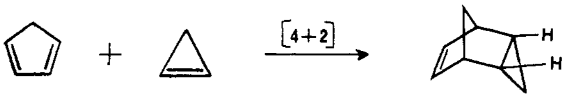
Received September 24, 1982

A study of the reactivity of 2-diazopropane with a series of diphenyl-substituted cyclopropenes has been carried out. The cycloadditions afford 1,5-diphenyl-2,3-diazabicyclo[3.1.0]hex-2-enes in high yield. Thermolysis of the diazabicyclohexene system for extended periods of time afforded a mixture of 1,3-dienes as well as a substituted bicyclo[1.1.0]butane. By studying the distribution of products as a function of time it was possible to show that the 2,3-diazabicyclohexene system first rearranges to an isomeric 1,2-diazabicyclo[3.1.0]hex-2-ene. This reaction was attributed to an initial [3 + 2] cycloreversion to produce a diazoalkene. Attack of the terminal nitrogen atom of the initially generated diazo group onto the neighboring double bond affords the bicyclic aziridine system. Reasonable mechanistic options for the 1,1-cycloaddition include a concerted pathway or a stepwise process. On further heating the 1,2-diazabicyclohexene ring regenerates the allyl-substituted diazoalkane. Loss of nitrogen produces a carbene which undergoes a hydrogen or vinyl shift to give the observed dienes. The formation of the bicyclo[1.1.0]butane ring can be viewed in terms of a process involving initial C–N bond cleavage of the 2,3-diazabicyclohexene to yield a diazenyl radical followed by nitrogen loss and radical coupling. In contrast to the thermal results, direct irradiation of the 2,3-diazabicyclohexene results in a [4 + 2] cycloreversion to give a 3,4-diaza-substituted 1,3,5-hexatriene derivative. The results obtained indicate that the total mechanistic picture for the thermal and photochemical decomposition of bicyclic pyrazolines can be changed dramatically by the presence of phenyl substituents.

Small-ring hydrocarbons possessing a strained π bond are of considerable interest, owing to their reactivity as well as their spectroscopic and structural properties.[1,2] Occasionally, such compounds are remarkably unreactive and stable, usually because reorganization to a less strained system must proceed via an even more highly strained transition state or because direct reaction is forbidden by orbital symmetry constraints.[3] More often, however, these systems undergo ready reaction with a variety of substrates. The cyclopropene ring is an especially good example of this phenomenon. [4 + 2] cycloaddition across the double bond in cyclopropene proceeds quite readily since it reduces ring strain by 26 kcal/mol.[4,5] The high reactivity of the cyclopropene π bond is demonstrated by the ease with which Diels–Alder additions take place. For example, at 0 °C cyclopropene and cyclopentadiene react rapidly and quantitatively to form a tricyclic adduct (i.e., 1, eq 1).[6] The reaction is completely stereospecific, and only the endo isomer is formed. The transition-state energy for this reaction, however, is very sensitive to steric factors as is indicated by the observation that 3,3-dimethylcyclopropene does not add, even at 100 °C.[7]



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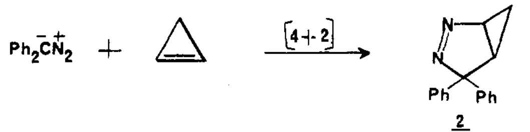

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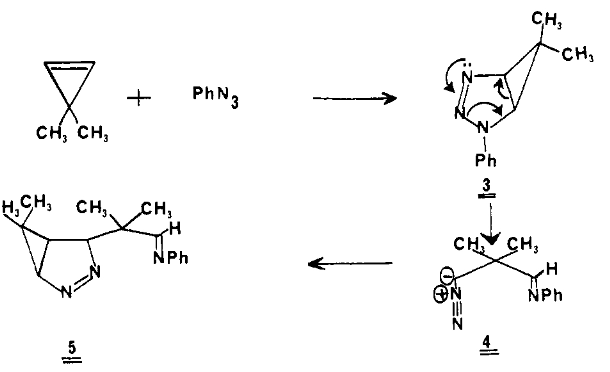

There are a number of reports in the literature which also describe 1,3-dipolar cycloadditions to cyclopropene.[8-30] Addition of diphenyldiazomethane to cyclopropene gives the pyrazoline 2[12] (eq 2), although a structure corresponding to a cyclopropyl to allyl rearrangement had originally been assigned.[6] Unrearranged products are also observed in the reactions of cyclopropenes with nitrile oxides[31,32] and nitrile imines.[32] The rates of these 1,3-dipolar cycloadditions are quite high, indicating that con-

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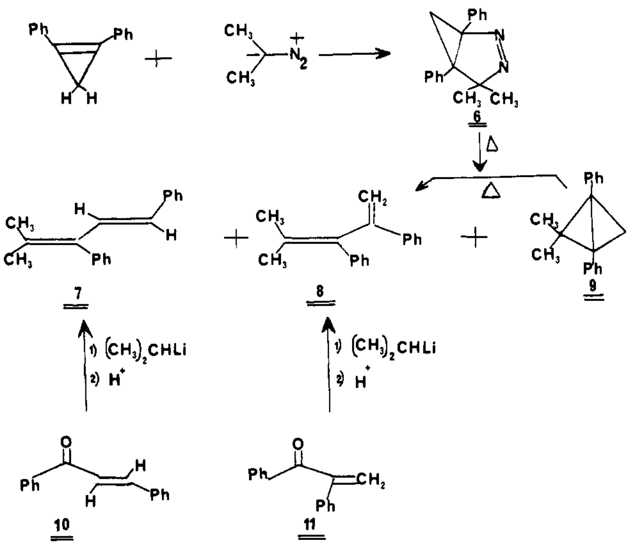
Scheme II



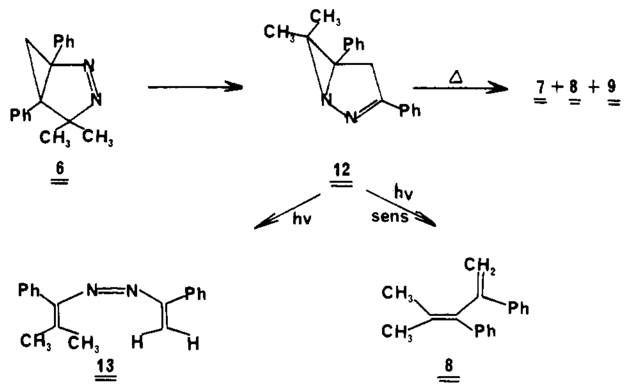
siderable strain in the olefin is relieved in the transition state for addition.[30] The initial cycloadducts often rearrange by valence bond tautomerization, and secondary products are frequently isolated. One interesting example involves the reaction of phenyl azide with 3,3-dimethylcyclopropene[30] (Scheme I). The reaction appears to give the normal cycloadduct which undergoes a 1,3-dipolar cycloreversion to give diazo compound **4**. Reaction of **4** with another molecule of cyclopropene produces the observed product **5**. An analogous cycloreversion has been observed by Franck-Neumann in the reaction of 1,2-dicarbomethoxy-3,3-dimethylcyclopropene with phenyl azide, but in that case the diazo compound could be isolated.[26]

In view of our interest in the cycloaddition behavior of cyclopropene derivatives,[33] we initiated a study dealing with the reaction of 2-diazopropane with several diphenylcyclopropenes. During the course of our studies we found that the initially formed 2,3-diazabicyclo[3.1.0]hex-2-enes undergo a novel rearrangement. This paper summarizes our observations in this area with particular reference to the mechanism of rearrangement.

Results

When 1,2-diphenylcyclopropene was treated with 2-diazopropane in ether solution at 25 °C, a clean cycloaddition reaction occurred to give pyrazoline **6** in 90% yield (Scheme II). The structure of **6** was suggested by the observation of a molecular ion at *m/e* 262 and an azo absorption in the infrared at 1600 cm^{-1}. The NMR of **6** showed two methyl singlets at δ 1.05 and 1.40, a pair of doublets at δ 0.65 (1 H, J = 6.0 Hz) and 1.55 (1 H, J = 6.0 Hz), and an aromatic multiplet at δ 6.7–7.3 (10H). Thermolysis of a sample of **6** in toluene at 130 °C for 10 h gave rise to a mixture consisting of (*E*)-1,3-diphenyl-4-methyl-1,3-pentadiene (**7**, 30%), 2,3-diphenyl-4-methyl-1,3-pentadiene (**8**, 32%), and 1,3-diphenyl-2,2-dimethylbicyclo[1.1.0]butane (**9**, 30%). The structures of **7** and **8** were established by comparison with independently synthesized samples. Treatment of 1,3-diphenyl-2-propenone (**10**) with isopropyllithium followed by dehydration of the resulting tertiary alcohol gave diene **7**. Structure **8** was prepared in a similar fashion by treating 1,2-diphenyl-2-propenone (**11**) with isopropyllithium and then dehydrating the resulting alcohol. The structure of **9** was established on the basis of its spectroscopic and chemical properties: NMR ($CDCl_3$, 90 MHz) δ 1.10 (s, 3 H), 1.30 (s, 3 H), 2.02 (d, 1 H, J = 1.5 Hz), 2.31 (d, 1 H, J = 1.5 Hz), 7.0–7.6 (m, 10 H). Further heating of **9** at 130 °C for 6 h gave **8** as the exclusive product in quantitative yield.

Scheme III



When the thermolysis of pyrazoline **6** was followed by NMR spectroscopy, a new compound (**12**) could be detected. This material was the exclusive product when a toluene solution of **6** was heated at 130 °C for 2 h rather than for 10 h. This new compound gave structures **7**–**9** (Scheme III) when heated for longer periods of time. A pure sample of **12** was obtained by fractional crystallization of the crude reaction mixture. This material is assigned as 3,5-diphenyl-6,6-dimethyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**12**); (mp 111–112 °C) on the basis of its spectroscopic properties which showed absorptions in the NMR at δ 1.02 (s, 3 H), 1.20 (s, 3 H), 2.97 (d, 1 H, J = 18.0 Hz), 3.27 (d, 1 H, J = 18.0 Hz), and 7.3–8.1 (m, 10 H). The UV spectrum of **12** showed an intense absorption band at 250 nm. A coupling constant of 18 Hz between the geminal protons is perfectly consistent with the above assignment.

Attention was next turned to the excited-state behavior of pyrazoline **6**. Photolysis of **6** with a Pyrex-filtered high-pressure mercury arc lamp for 2 h gave rise to a single photoisomer whose structure is assigned as 3,4-diaza-6-methyl-2,5-diphenyl-1,3,5-hexatriene (**13**): NMR ($CDCl_3$, 90 MHz) δ 1.60 (s, 3 H), 1.90 (s, 3 H), 4.35 (s, 1 H), 5.02 (s, 1 H), 6.8–7.8 (m, 10 H). No products corresponding to the loss of nitrogen were observed. The formation of **13** from **6** was due to the initial conversion of **6** to **12** which was further transformed to **13** under the reaction conditions. This was established by studying the distribution of products as a function of time. At short exposures, pyrazoline **6** gave **12** as the exclusive photoproduct. The triplet-sensitized (benzophenone) irradiation of **6** also produced **12**. In contrast to the direct photolysis, however, the sensitized irradiation of **12** afforded diene **8** as the exclusive photoproduct.

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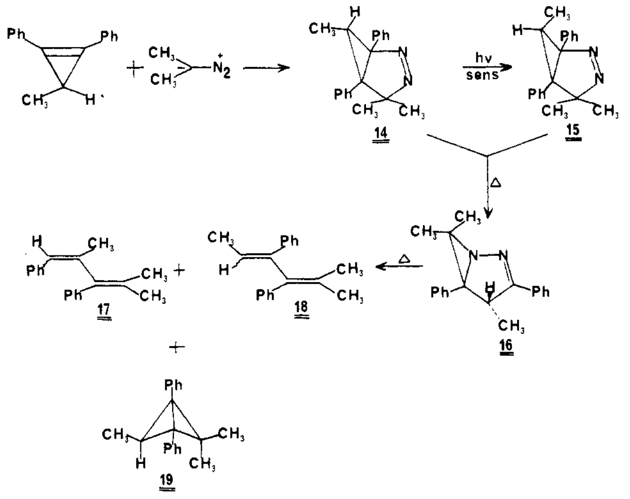
Scheme IV



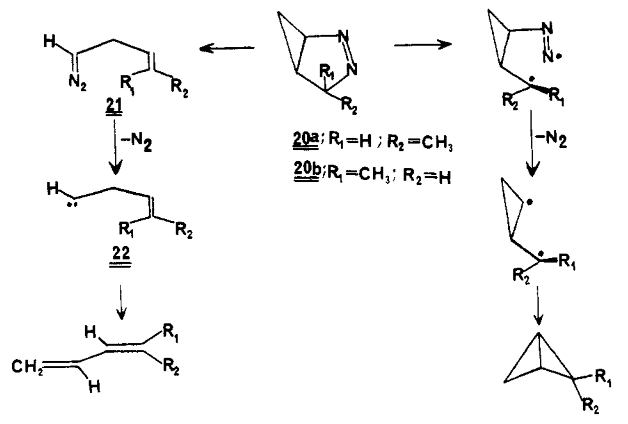
A related set of results was encountered when 1,2-diphenyl-3-methylcyclopropene was allowed to react with 2-diazopropane. In this case the major product isolated (77%) was a crystalline solid (mp 93–94 °C) whose structure was assigned as *exo*-1,5-diphenyl-4,4,6-trimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (**14**, Scheme IV). As is the case with most 1,3-dipolar cycloadditions,[34] the 1,3-dipole added from the least hindered side of the π bond to give the exo isomer. This assignment was supported by the epimerization of **14** to the corresponding endo isomer **15** via a sensitized irradiation (benzophenone). The structure of the endo isomer was unequivocally established by an X-ray single-crystal structure analysis. Crystals of **15** were monoclinic, space group $C2/c$, with unit cell parameters a = 19.000 (3) Å, b = 9.368 (1) Å, c = 22.231 (2) Å, β = 124.77 (1)°, V = 3250.7 (7) Å^3, d_{calcd} = 1.13 g cm^{-3}; $F(000)$ = 1184.0, and Z = 8. The intensity data were measured on a Nicolet R_3 four-circle diffractometer using Cu Kα radiation. The structure was derived by using direct methods and refined by least-squares methods to give an R value of 0.055 for all the data.

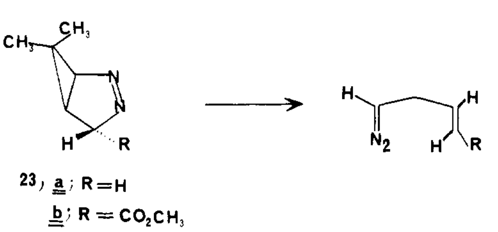
We have also examined the thermolysis of both the *exo*- (**14**) and *endo*-pyrazolines (**15**) and find that both of these compounds produce a 9:1 mixture of *exo*- (**16**) and *endo*-3,5-diphenyl-4,6,6-trimethyl-1,2-diazabicyclo[3.1.0]hex-2-ene on heating at 130 °C for 2 h. When the thermolysis of **14** (or **15**) was carried out in toluene at 130 °C for 5 h, a mixture of 1,3-diphenyl-2,4-dimethyl-1,3-pentadiene (**17**, 43%), 3,4-diphenyl-2-methyl-2,3-hexadiene (**18**, 44%), and 1,3-diphenyl-2,4,4-trimethylbicyclo[1.1.0]butane (**19**, 5%) was isolated. The structures of these compounds were assigned on the basis of their spectral properties (see Experimental Section). Heating a sample of **16** in toluene under comparable conditions also produced the same mixture of hydrocarbons.

Discussion

The reaction products obtained on thermal or photochemical decomposition of derivatives of 2,3-diazabicyclo[3.1.0]hex-2-ene differ fundamentally from those of other bicyclic 1-pyrazolines.[35] Eaton, Bergman, and Hammond reported that the decomposition of diazabicyclohexene **20** produced products which were readily explained in terms of the initial formation of a diazoalkene **21**, followed by loss of nitrogen to give the carbene **22** and subsequent rearrangement to yield olefins[11] (Scheme V). Thus **20a** gave *trans*-1,3-pentadiene while **20b** afforded *cis*-1,3-pentadiene. This was interpreted in terms of the intermediacy of a carbene which undergoes hydrogen or vinyl migration. The formation of the bicyclo[1.1.0]butane ring was viewed in terms of a process involving initial carbon–nitrogen bond cleavage to yield a diazenyl radical followed by loss of nitrogen to give a cyclopropyl diradical.[12] This species undergoes subsequent ring closure to give the bicyclobutane. The first reaction step involving formation of the diazoalkene can be regarded as the [3 + 2] cycloreversion of a thermally allowed [$_\pi4_s$ + $_\pi2_s$] cycloaddition. This reaction represents an interesting example of a 1,3-dipole metathesis process since the diazoalkane obtained is different from the one used to synthesize the pyrazoline.[36] The driving force for the reaction is the relief of ring strain although conjugation gain is another factor which may assist in accelerating the fragmentation. The cycloreversion propensity of 2,3-diazabicyclohexenes is known to be greatly enhanced when electron-withdrawing substituents are present at the incipient olefin moiety. This effect parallels a well-known phenomenon in the 1,3-dipolar cycloaddition process. For example, pyrazoline **23a** is stable up to 125 °C, but **23b** undergoes cycloreversion at temperatures as low as 0 °C[30] (eq 3).

Scheme V





(3)

The results that we have encountered with the diphenyl-substituted pyrazolines **6**, **14**, and **15** contrast strongly with those previously reported. Our results indicate that the total mechanistic picture for the decomposition of derivatives of 2,3-diazabicyclo[3.1.0]hex-2-ene can be changed dramatically by the presence of phenyl substituents. Thus, formation of the isomeric 1,2-diazabicyclo[3.1.0]hex-2-ene system (i.e., **12** or **16**) as the exclusive thermal product requires a modification of the previous mechanistic speculation. We have found that when the thermolysis of **6** or **14** was followed by NMR spectroscopy, a pink coloration developed which gradually faded on extended heating. In addition, a new band was detected in the infrared at 1984 cm^{-1} which is consistent with the intermediacy of a phenyl diazoalkene. The fact

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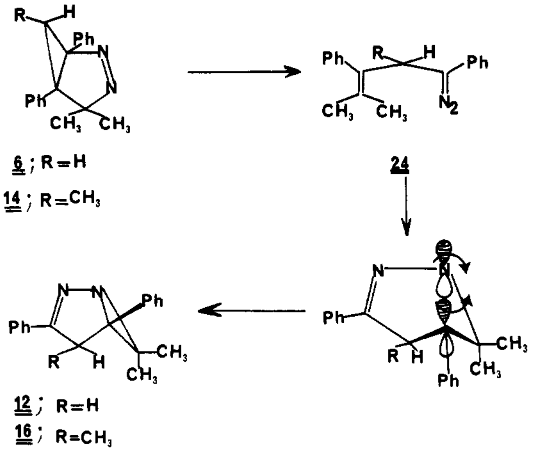
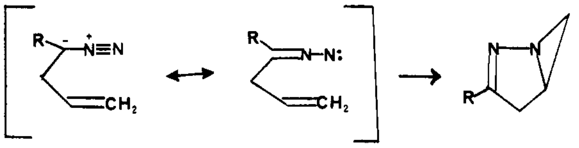
Scheme VI



that we were unable to isolate this intermediate suggests that the 1,3-dipolar cycloreversion is the rate-determining step.

The additions of diazoalkanes to olefins are among the most thoroughly studied 1,3-dipolar cycloadditions.[34,37-39] The reactions of simple diazoalkanes are HO(1,3-dipole)-LU(dipolarophile) controlled.[40,41] 3-Substituted pyrazolines are the major products produced, a result of union of the larger diazoalkane HO coefficient on carbon with that of the larger dipolarophile LU coefficient on the unsubstituted carbon.[40] Recent work from our laboratory[42] as well as studies by Miyashi and Mukai[43] have shown that intramolecular 1,1-cycloaddition of diazoalkenes can compete with the normal 1,3-addition mode when certain geometric constraints are imposed. Thus, various allyl-substituted diazomethanes have been found to undergo a formal nitrene-type 1,1-cycloaddition to give 1,2-diazabicyclo[3.1.0]hex-2-enes on heating (eq 4).



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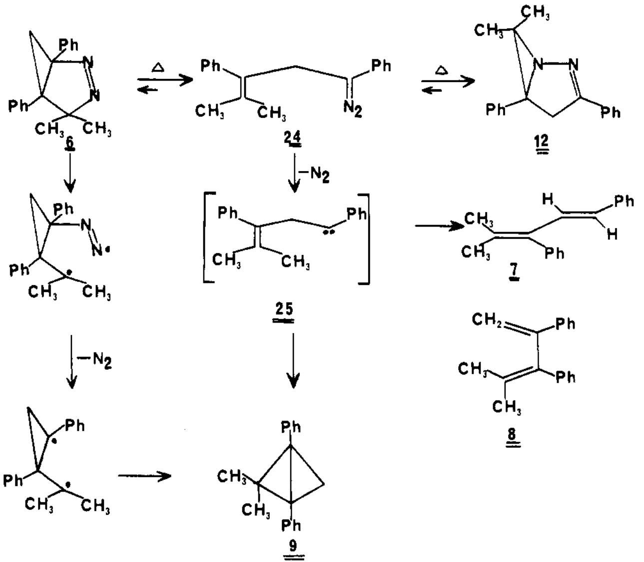
Scheme VII



A mechanism analogous to that described above nicely accounts for the formation of 1,2-diazabicyclohexene **12** or **16** from the thermolysis of pyrazoline **6** or **14** (Scheme VI). Attack of the terminal nitrogen atom of the initially generated diazo group on the neighboring double bond affords the bicyclic aziridine ring system. Reasonable mechanistic options for the 1,1-cycloaddition of diazoalkene **24** include a concerted pathway or a stepwise process. The concerted path would parallel the stereospecific addition of singlet nitrenes to olefins which proceeds with retention of stereochemistry about the double bond.[44] Stepwise nucleophilic attack of the terminal double bond on the electron-deficient nitrogen atom of diazoalkene **24** can generate a six-membered-ring dipole which contains an aza-allylic carbanion as well as a secondary carbonium ion. Collapse of this new 1,3-dipole will generate the diazabicyclohexane ring system. The overall reaction is similar to that involved in the intramolecular 1,1-cycloaddition of nitrile ylides[45,46] and nitrile imines.[47,48]

Inspection of molecular models of the allyl-substituted diazoalkane system indicates that the normal "two-plane" orientation approach[34] of the diazo group and the allyl π system is impossible as a result of the geometric restrictions imposed on the system. Consequently, the normal mode of 1,3-dipolar addition does not occur here. Such geometric restriction alone, however, is not sufficient for the 1,1-cycloaddition process to occur. Thus, no 1,1-cycloaddition has been reported for allyldiazomethane[24,49] and its derivatives bearing α-alkyl[36,50] and π-electron withdrawing groups.[26,29,51] Formation of the 1,2-diazabicyclohexene ring seems to be limited to α-phenyl-substituted derivatives.[42,43]

The diazo group possesses two mutually perpendicular π systems. One of these (π_z) is delocalized over the entire π framework and, like the allyl anion, contains four electrons. The other π system (i.e., π_y) is localized on the two nitrogen atoms, each of which furnishes an electron. The terminal nitrogen atom also bears a lone pair of electrons which is sp hybridized. The nitrene form of a diazo compound could become quite important if the R group is π donating and σ withdrawing. In fact, a phenyl group has such characteristics (i.e., $\sigma_R = -0.11$, and $\sigma_I = 0.10$). The nitrene character of the diazo group, like a carbene, is derived from the mutually perpendicular frontier molecular orbitals which are energetically accessible and possess sizable eigenvectors at the atomic center. In the case of diazo compounds, this means that the π_z and $\pi_y{}^*$ orbitals should have sizable eigenvectors on N_1 and that the π_z–$\pi_y{}^*$ energy gap should be small. MO calculations at the 4-31G level[52] indicate that the energy gap for planar aryldiazo-

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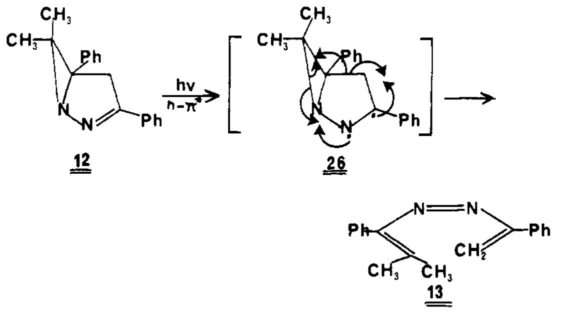
methanes is about 1 eV smaller than for other diazo species. In order for the 1,1-cycloaddition to proceed effectively, it is necessary that the diazo group possess a high-lying occupied π_z orbital with a sizable coefficient on N_1. The MO calculations indicate that a phenyl group fulfills these requirements whereas hydrogen, alkyl, or π-electron-withdrawing groups do not. Thus, the energetics and shapes of the highest occupied molecular orbital of the delocalized π system will dictate the ultimate outcome of the thermal reaction of the bicyclic 1-pyrazoline ring system.

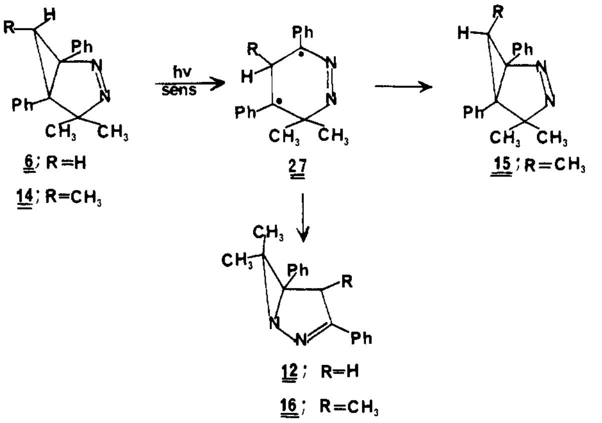
Earlier work in our laboratory[42] as well as studies by Miyashi and Mukai[43] have established the reversibility of the 1,1-cycloaddition between the diazoalkene and the 1,2-diazabicyclohexene ring. This reversibility would nicely account for the formation of dienes **7** and **8** as well as bicyclobutane **9** from the thermolysis of **12** (Scheme VII). Extrusion of nitrogen from diazo compound **24** will give a carbene (**25**) which can rearrange by either a hydrogen or vinyl shift. The bicyclo[1.1.0]butane could be derived by intramolecular addition of the carbene across the neighboring π bond. Thermochemical calculations suggest that the opening of pyrazolines to diazo compounds is approximately thermoneutral.[30] If the initially generated diazo species **24** is also in equilibrium (to a very small degree) with pyrazoline **6**,[56] then the formation of **9** from **12** could be explained in terms of diazenyl and cyclopropyl diradicals. An analogous mechanism would rationalize the formation of **17**–**19** from the thermolysis of **14**–**16**.

In marked contrast to the thermal results, we have found that photolysis of the 1,2-diazabicyclohexene ring (i.e., **12**) results in a [4 + 2] cycloreversion to give diazahexatriene **13** (eq 5). This is significantly different from the [3 + 2] cycloreversion reaction which occurs when pyrazoline **6** is irradiated.[57] The [4 + 2] cycloreversion represents the reverse of the photo-Diels–Alder reaction of hexa-1,3,5-trienes.[58] Rearrangements of this type are known for both nitrogen- and oxygen-substituted bicyclo[3.1.0]hex-2-enes.[14,59-61] The initial step in the [3 + 2] cycloreversion of **6** involves cleavage of the N_3–C_4 bond whereas in the [4 + 2] cycloreversion of **12** scission of the C_4–C_5 bond takes place. One may envisage the photolysis of **12** as involving an n–π^* transition which will lead to a species resembling structure **26**, where the nonbonding orbital on nitrogen contains only one electron. The electron that was promoted to the antibonding π^* orbital will partially reside on the carbon atom. The remaining nonbonding electron on nitrogen can overlap with the aziridinyl bent bond and facilitate bond scission. This is somewhat analogous to the ring opening of the cyclopropyl carbinyl to the 4-butenyl radical.[62] The facile aziridine ring opening is a manifestation of a π^*-assisted cleavage, of which there are a growing number of examples.[63] This is probably the major factor responsible for the difference in photobehavior of the two diazabicyclohexenes.



(5)

Scheme VIII



Another point worth discussing deals with the sensitized irradiation of the 2,3-diazabicyclohexene system. The triplet-induced extrusion of nitrogen from cyclic azoalkanes is a well-documented reaction.[64-67] Recent fascinating examples include the formation of the prismanyl,[68] the norbornadienyl and quadricyclenyl,[69] and the barrelenyl diradicals[70] via denitrogenation of the respective azoalkane precursors. We have found that in contrast to the direct irradiation, the benzophenone-sensitized photolysis of **6** gave **12**, as the exclusive photoproduct (Scheme VIII). Denitrogenation did not take place. In order to obtain a more satisfactory picture of the overall reaction, we followed the course of the photorearrangement of **6** by NMR and IR spectroscopy. Unlike the direct photolysis, we were unable to detect the presence of diazoalkene **24** in the crude photolysate. Moreover, with pyrazoline **14**, epimerization to the endo isomer **15** occurs prior to formation of diazabicyclohexene **16**. These reactions probably proceed by cleavage of the central bond to give diradical **27** which undergoes ring flipping followed by a subsequent ring closure. Coupling of diradical **27** can also occur to give the rearranged product. Although the triplet-sensitized

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[52] Ab initio calculations at the 4-31G level[53] were carried out by Dr. T. Fukunaga (Du Pont Co.) using the program GAMESS[54] and standard geometries. The results of these calculations will be published elsewhere.[55]

[53] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.

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[56] For a related suggestion see: Lahti, P. M.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 7011.

[57] The formation of **12** from the irradiation of **6** involves initial conversion to diazoalkene **24** followed by the 1,1-cycloaddition reaction. This interpretation is supported by the appearance of a diazo band in the infrared and formation of a distinct pink coloration of the photolysate.

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behavior of these bicyclic pyrazolines is unusual, a few examples have been reported in the literature in which azo alkanes undergo [1,3] sigmatropic shifts rather than extrude molecular nitrogen.[71–73]

In conclusion, energization of the 1,5-diphenyl-2,3-diazabicyclo[3.1.0]hex-2-ene system has led to several distinct products. Such divergent chemical behavior makes the bicyclic pyrazoline **6** a unique system and underscores its novelty. Our results indicate that the total mechanistic picture for the photochemical decomposition of derivatives of bicyclic pyrazolines can be changed dramatically by the presence of phenyl substituents. We are continuing to investigate both the synthetic and mechanistic aspect of 2,3-diazabicyclohexene photochemistry and will report additional findings at a later date.

Experimental Section[74]

Reaction of 1,2-Diphenylcyclopropene with 2-Diazopropane. A solution containing 9.0 g of 1,2-diphenylcyclopropene and 10.0 g of 2-diazopropane in 100 mL of ether was stirred at −78 °C for 2 h. The reaction mixture was allowed to warm to room temperature and was stirred for an additional 18 h. The solvent was removed under reduced pressure, and the oily residue was crystallized from hexane to give 1,5-diphenyl-4,4-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (**6**, 90%) as a white crystalline solid: mp 101–102 °C; IR (KBr) 3050, 2980, 2900, 1600, 1440, 1240 cm^{-1}; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.65 (d, 1 H, J = 6.0 Hz), 1.05 (s, 3 H), 1.40 (s, 3 H), 1.55 (d, 1 H, J = 6.0 Hz), 6.7–7.3 (m, 10 H); UV (95% ethanol) 330 nm (ϵ 260); mass spectrum, *m/e* 262, 219 (base), 204, 191, 143. Anal. Calcd for C$_{18}$H$_{18}$N$_2$: C, 82.40, H, 6.92; N, 10.68. Found: C, 82.19; H, 6.96; N, 10.67.

Thermal Rearrangement of 1,5-Diphenyl-4,4-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (6). A solution containing 0.5 g of **6** mL of toluene was heated in a sealed tube at 130 °C for 2 h. Removal of the solvent under reduced pressure left a yellow oil which was crystallized from hexane to give 3,5-diphenyl-6,6-dimethyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**12**): 80% yield; mp 111–112 °C; IR (KBr) 3080, 3050, 2950, 1540, 1440, 1240, 840 cm^{-1}; ^{1}H NMR (90 MHz, benzene-d_6) δ 1.02 (s, 3 H), 1.20 (s, 3 H), 2.97 (d, 1 H, J = 18.0 Hz), 3.27 (d, 1 H, J = 18.0 Hz), 7.3–8.1 (m, 10 H); UV (95% ethanol) 250 nm (ϵ 11 300); mass spectrum, *m/e* 234, 219 (base), 204, 191. Anal. Calcd for C$_{18}$H$_{18}$N$_2$: C, 82.40; H, 6.92; N, 10.68. Found: C, 82.33; H, 6.94; N, 10.65.

Thermolysis of 3,5-Diphenyl-6,6-dimethyl-1,2-diazabicyclo[3.1.0]hex-2-ene (12). A solution containing 500 mg of **12** in 10 mL of toluene was heated in a sealed tube at 130 °C for 10 h. Removal of the solvent under reduced pressure left a clear oil which was subjected to silica gel chromatography with hexane as the eluent. The three-component mixture (1:1:1) was eventually separated to give three compounds. The first compound was identified as (*E*)-1,3-diphenyl-4-methyl-1,3-pentadiene (**7**) on the basis of its spectral properties and by comparison with an independently synthesized sample: bp 140 °C (0.12 mm); IR (neat) 3050, 2800, 1590, 1500, 1030, 830 cm^{-1}; ^{1}H NMR (90 MHz, benzene-d_6) δ 1.50 (s, 3 H), 1.80 (s, 3 H), 6.21 (d, 1 H, J = 15.0 Hz), 7.0–7.3 (m, 10 H), 7.50 (d, 1 H, J = 15.0 Hz); UV (95% ethanol) 290 (ϵ 26 500), 232 (27 000); mass spectrum, *m/e* 234 (M$^+$ and base), 219, 205, 191, 77. Anal. Calcd for C$_{18}$H$_{18}$: C, 92.26; H, 7.74. Found: C, 92.08; H, 7.78.

The structure of this material was further verified by comparison with an authentic sample. To a solution containing 1.0 g of 1,3-diphenyl-2-propen-1-one (**10**) in 10 mL of hexane was added 1.2 equiv of freshly prepared isopropyllithium under a nitrogen atmosphere. The mixture was allowed to stir at 25 °C for 12 h and was then quenched with a saturated ammonium chloride solution. The organic layer was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was chromatographed on a silica gel column with a 2% acetone–hexane mixture as the eluent. The first component isolated from the column contained 0.5 g of 1,3-diphenyl-4-methyl-1-pentanone as a pale yellow oil: ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.80 (d, 3 H, J = 6.0 Hz), 1.02 (d, 3 H, J = 6.0 Hz), 1.8–2.1 (m, 1 H), 3.2–3.4 (m, 3 H), 7.2–8.0 (m, 10 H). The second fraction collected from the column contained 0.3 g of (*E*)-1,3-diphenyl-4-methyl-1-penten-3-ol as a pale oil: IR (neat) 3500, 3050, 2980, 1600, 940 cm^{-1}; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.70 (d, 3 H, J = 6.0 Hz), 0.90 (d, 3 H, J = 6.0 Hz), 1.70 (s, 1 H), 2.0–2.3 (m, 1 H), 6.50 (s, 2 H), 7.0–7.7 (m, 10 H). To a mixture containing 0.3 g of this compound and 0.3 g of pyridine in 25 mL of benzene was added 0.4 g of thionyl chloride at 0 °C. After being stirred for 12 h at 25 °C, the mixture was poured onto cracked ice and was acidified with a cold 2% aqueous hydrochloric acid solution. The mixture was extracted with ether which was then washed with a sodium bicarbonate solution, water, and a saturated salt solution. The ether layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resulting oil was chromatographed on silica gel using hexane to give (*E*)-1,3-diphenyl-4-methyl-1,3-pentadiene (**7**) which was identical in every detail with a sample obtained from the thermolysis of **12**.

The second material isolated from the chromatographic separation of the material obtained from the thermolysis of **12** was a clear oil whose structure was assigned as 2,3-diphenyl-4-methyl-1,3-pentadiene (**8**) on the basis of its spectral properties and by comparison with an independently synthesized sample: bp 110 °C (0.04 mm); IR (neat) 3100, 2900, 1600, 1440, 900 cm^{-1}; ^{1}H NMR (90 MHz, benzene-d_6) δ 1.60 (s, 3 H), 1.70 (s, 3 H), 5.21 (d, 1 H, J = 1.5 Hz), 5.72 (d, 1 H, J = 1.5 Hz), 6.8–7.9 (m, 10 H); UV (95% ethanol) 250 nm (ϵ 33 400); mass spectrum, *m/e* 234 (M$^+$, base), 219, 115, 77. Anal. Calcd for C$_{18}$H$_{18}$: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.68.

The structure of this material was further verified by comparison with an independently synthesized sample. A solution containing 40 mL of a 1.6 M solution of isopropyllithium tetramethylethylenediamine complex in ether at −55 °C was added to 1.0 g of 1,2-diphenyl-2-propen-1-one (**11**) in 25 mL of ether at −106 °C. The mixture was allowed to stir at −78 °C for 2.5 h and was then quenched with a saturated ammonium chloride solution. The ether solution was washed with water and was dried over magnesium sulfate. Removal of the solvent left an oil which was chromatographed on a silica gel column with a 2% ethyl acetate–hexane mixture as the eluent. The first component (60%) was a crystalline solid (mp 64–65 °C) whose structure was assigned as 1,2-diphenyl-4-methylpentan-1-one: ^{1}H NMR (CDCl$_3$, 90 MHz) δ 0.95 (d, 3 H, J = 8.0 Hz), 1.02 (d, 3 H, 8.0 Hz), 1.40–1.70 (m, 2 H), 2.0–2.3 (m, 1 H), 4.65 (t, 1 H, J = 6.0 Hz), 7.1–8.1 (m, 2 H). The second component isolated from the column contained 350 mg of 2,3-diphenyl-4-methyl-1-penten-3-ol as a clear oil: IR (neat) 3600, 3050, 2900, 1600, 900 cm^{-1}; ^{1}H NMR (CDCl$_3$, 90 MHz) 0.70 (d, 3 H, J = 6.0 Hz), 1.15 (d, 3 H, J = 6.0 Hz), 1.65 (s, 1 H), 2.2–2.6 (m, 1 H), 5.10 (d, 1 H, J = 1.0 Hz), 5.50 (d, 1 H, J = 1.0 Hz), 7.0–7.6 (m, 10 H). To a mixture containing 350 mg of the above material and 500 mg of pyridine in 25 mL of benzene was added 700 mg of thionyl chloride at 0 °C. After being stirred at 0 °C for 2 h, the mixture was allowed to stir at 25 °C for an additional 12 h. The solution was poured onto cracked ice, acidified with a cold 20% hydrochloric acid solution, and washed with a saturated sodium bicarbonate solution, followed by a water wash and then a saturated salt solution wash. The ether layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resulting oil was chromatographed on silica gel with hexane as the eluent to give 2,3-diphenyl-4-methyl-1,3-pentadiene (**8**) which was identical in every detail with a sample obtained from the thermolysis of **12**.

The third component isolated from the chromatographic separation of the material isolated from the thermolysis of **12** could not be completely separated from dienes **7** and **8**. Its NMR

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(74) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. The infrared absorption spectra were determined on a Perkin-Elmer 467 infrared spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer by using 1-cm matched cells. The proton magnetic resonance spectra were determined at 90 MHz by using a Varian EM-390 spectrometer. Mass spectra were determined with a Finnigan 4000 mass spectrometer at an ionizing voltage of 70 eV.

spectrum is most consistent with its assignment as 1,3-diphenyl-2,2-dimethylbicyclo[1.1.0]butane (9): ^{1}H NMR (90 MHz, benzene-d_6) δ 1.10 (s, 3 H), 1.30 (s, 3 H), 2.02 (d, 1 H, J = 1.5 Hz), 2.31 (d, 1 H, J = 1.5 Hz), 7.0–7.6 (*m*, 10 H). Heating this material in toluene at 130 °C for 6 h gave 2,3-diphenyl-4-methyl-1,3-pentadiene (8) as the exclusive product in quantitative yield.

Direct Irradiation of 1,5-Diphenyl-4,4-dimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (6). A solution containing 0.5 g of 6 in 250 mL of benzene was irradiated in a Pyrex immersion well for 2 h. Removal of the solvent left a somewhat labile yellow oil whose structure is assigned as 2,5-diphenyl-6-methyl-3,4-diaza-1,3,5-hexatriene (13) on the basis of its spectral data: IR (neat) 3070, 3050, 2250, 1680, 1600, 1380 cm^{-1}; ^{1}H NMR (90 MHz, benzene-d_6) δ 1.60 (s, 3 H), 1.90 (s, 3 H), 4.35 (s, 1 H), 5.02 (s, 1 H), 6.8–7.8 (m, 10 H); mass spectrum, *m/e* 159, 103 (base), 77; UV (95% ethanol) 245 nm (ϵ 15600). Direct irradiation of 3,5-diphenyl-6,6-dimethyl-1,2-diazabicyclo[3.1.0]hex-2-ene (12) also led to the same product in 88% yield. All attempts to further purify this material led to its extensive decomposition. The triplet-sensitized irradiation of 6 with benzophenone as the sensitizer produced 3,5-diphenyl-6,6-dimethyl-1,2-diazabicyclohexene 12 as the major product in 90% yield. No signs of the diazahexatriene 13 could be detected in the crude photolysate. The sensitized photolysis of 12 afforded an 85% yield of 2,3-diphenyl-4-methyl-1,3-pentadiene (8) as the exclusive photoproduct.

Reaction of 1,2-Diphenyl-3-methylcyclopropene with 2-Diazopropane. A mixture containing 8.0 g of 1,2-diphenyl-3-methylcyclopropene and 7.0 g of 2-diazopropane in 100 mL of ether was allowed to stir at −78 °C for 2 h and at 0 °C for 5 h. At the end of this time the mixture was stirred at 25 °C for an additional 12 h. Removal of the solvent under reduced pressure left an oil which was crystallized from hexane to give *exo*-1,5-diphenyl-4,4,6-trimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (14, 77%) as a white crystalline solid: mp 93–94 °C; IR (KBr) 3070, 3050, 2990, 2950, 1598, 1527, 1458, 1381, 1358, 1237, 1020, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.05 (m, 4 H), 1.52 (s, 3 H), 1.58 (s, 3 H), 6.8–7.8 (m, 10 H); UV (95% ethanol) 330 nm (ϵ 250); mass spectrum, *m/e* 276 (M$^+$), 248, 219, 205, 178, 115 (base), 91, 77. Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.49; H, 7.33; N, 10.14.

Triplet-Sensitized Irradiation of *exo*-1,5-Diphenyl-4,4,6-trimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (14). A solution containing 300 mg of 14 and 315 mg of benzophenone in 250 mL of benzene was irradiated through a uranium-glass filter sleeve for 3 h. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column with a 10% ether–hexane mixture as the eluent. The major fraction (40%) obtained was a crystalline solid (mp 102–103 °C) whose structure was assigned as *endo*-1,5-diphenyl-4,4,6-trimethyl-2,3-diazabicyclo[3.1.0]hex-2-ene (15) on the basis of its spectral data and by an X-ray crystal structure analysis: IR (KBr) 3075, 3045, 3000, 2950, 1600, 1492, 1452, 1380, 1248, 738, 688 cm^{-1}; ^{1}H NMR (90 MHz, benzene-d_6) δ 0.85 (*d*, 3 H, J = 6.4 Hz), 0.93 (s, 3 H), 1.39 (s, 3 H), 1.94 (q, 1 H, J = 6.4 Hz), 6.9–7.3 (m, 6 H), 7.6–7.8 (m, 4 H); UV (95% ethanol) 220 nm (ϵ 12700), 260 (1300), 330 (370); mass spectrum, *m/e* 276 (M$^+$), 248, 238, 228 (base), 205, 155, 138, 116. Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.49; H, 7.30; N, 10.11.

Colorless crystals were grown from hexane. A suitable crystal of approximately 0.2 × 0.2 × 0.3 mm was mounted on a quartz fiber with epoxy cement such that the longest crystal dimension was parallel to the fiber axis. Unit cell parameters were determined on a Nicolet R_3 four-circle diffractometer using Ni-filtered Cu Kα radiation with a takeoff angle of 6.0°. Fifteen reflections were machine centered and used in the least-squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were a = 19.000 (3) Å, b = 9.368 (1) Å, c = 22.231 (2) Å, β = 124.77 (1)°, V = 3250.7 (7) Å^3, d_{calcd} = 1.13 g cm^{-3}, $F(000)$ = 1184.0, Z = 8, and space group *C*2/*c*.

Intensity data were collected by using the 2θ–θ scan technique with a variable scan rate of 4–29.3° min^{-1}. A scan width of 2.0° was sufficient to collect all of the peak intensity. Control reflections, monitored after each set of 83 scans, showed no significant change during the course of data collection. Lorentz and polarization corrections were made in the usual way. No absorption correction was applied. Of the total of 1876 reflections collected with 4.0° ≤ 2θ ≤ 109.0°, 1282 were found to be unique and have $I \geq 3\sigma(I)$. The structure was solved by direct methods with the SHELX-76 program. Following anisotropic refinement of the backbone atoms, all hydrogens were located in a weighted electron density difference Fourier synthesis. Refinement of the hydrogens with isotropic thermal parameters reduced the residuals to R = 0.055 and R_w = 0.039, where $R_w = \sum w^{1/2}(F_o - F_c)/\sum w^{1/2}F_o$. The carbon–hydrogen bond distances were constrained to 1.080 (6) Å. The largest peak of the final difference Fourier map was 0.15 e Å^{-3}.[75]

Thermolysis of 1,5-Diphenyl-4,4,6-trimethyldiazabicyclo[3.1.0]hex-2-ene. A solution containing 2.02 g of *exo*-14 in 20 mL of toluene was heated in a sealed tube at 130 °C for 5 h. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed on a silica gel column with hexane as the eluent. The first fraction eluted from the column contained 1.064 g (57%) of a clear oil whose NMR spectrum showed that it contained a mixture of (*E*)- and (*Z*)-1,3-diphenyl-2,4-dimethyl-1,3-pentadiene (17, 2:1 ratio) as well as 1,3-diphenyl-2,4,4-trimethylbicyclo[1.1.0]butane (19). The (*E*) and (*Z*)-dienes could not be completely separated from each other but showed signals in the ^{1}H NMR ($CDCl_3$, 90 MHz) for the *E* isomer at δ 1.60 (s, 3 H), 1.75 (s, 3 H), 1.80 (s, 3 H), 6.30 (m, 1 H), and 6.8–7.9 (m, 10 H) while the *Z* isomer contained signals at δ 1.60 (s, 3 H), 1.75 (s, 3 H), 1.80 (s, 3 H), 6.45 (m, 1 H), and 6.8–7.9 (m, 10 H). Bicyclo[1.1.0]butane 19 was a colorless oil which resisted all attempts at crystallization: IR (neat) 2980, 1600, 1500, 1440, 740 cm^{-1}; ^{1}H NMR (90 MHz, benzene-d_6) δ 0.99 (d, 3 H, J = 6.0 Hz), 1.06 (s, 3 H), 1.14 (s, 3 H), 2.10 (q, 1 H, J = 6.0 Hz), 7.0–7.4 (m, 10 H); mass spectrum, *m/e* 248 (M$^+$), 233, 119 (base), 84; ^{13}C NMR (benzene-d_6) δ 8.92 (q), 11.54 (q), 17.79 (q), 31.65 (s), 35.49 (d), 41.80 (s).

The second fraction isolated from the column contained 220 mg of a colorless oil whose structure was assigned as 3,4-diphenyl-2-methyl-2,3-hexadiene (18) on the basis of its spectral properties: IR (neat) 3080, 3005, 2930, 2870, 1598, 1574, 1490, 1369, 748, 690 cm^{-1}; ^{1}H NMR (90 MHz, benzene-d_6) δ 1.70 (d, 3 H, J = 7.4 Hz), 1.73 (s, 3 H), 1.77 (s, 3 H), 5.98 (q, 1 H, J = 7.4 Hz), 6.9–7.5 (m, 10 H); UV (95% ethanol) 245 nm (ϵ 15800).

The third fraction isolated from the column contained 632 mg (31%) of a 9:1 mixture of *exo*- (16) and *endo*-3,5-diphenyl-4,6,6-trimethyl-1,2-diazabicyclo[3.1.0]hex-2-ene. The exo isomer 16 was obtained as a colorless solid: mp 99–100 °C; IR (KBr) 3075, 3055, 3020, 2950, 2860, 1600, 1560, 1498, 1452, 1445, 762, 690 cm^{-1}; NMR (90 MHz, benzene-d_6) δ 1.08 (s, 3 H), 1.13 (d, 3 H, J = 7.4 Hz), 1.17 (s, 3 H), 3.53 (q, 1 H, J = 7.4 Hz), 7.0–7.3 (m, 6 H), 7.3–7.5 (m, 2 H), 7.5–7.7 (m, 2 H); UV (95% ethanol) 250 nm (ϵ 10100); mass spectrum, *m/e* 276 (M$^+$), 248, 173, 158, 141, 117, 105, 91, 77. Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; N, 7.29; N, 10.11. Found: C, 82.97; N, 7.26; N, 9.82.

Thermolysis of a sample of the endo isomer 15 in a sealed tube at 130 °C for 80 h produced a mixture of 17 (43%), 18 (44%), and 19 (5%).

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health.

Registry No. **6**, 85267-78-3; (*E*)-**7**, 85267-79-4; **8**, 85267-80-7; **9**, 85267-81-8; (*E*)-**10**, 614-47-1; **11**, 4452-11-3; **12**, 85267-82-9; **13**, 85267-83-0; **14**, 85317-07-3; **15**, 85317-08-4; *endo*-**16**, 85267-84-1; *exo*-**16**, 85267-85-2; (*E*)-**17**, 85267-86-3; (*Z*)-**17**, 85267-87-4; **18**, 85267-88-5; **19**, 85267-89-6; 1,3-diphenyl-4-methyl-1-pentanone, 85267-90-9; (*E*)-1,3-diphenyl-4-methyl-1-penten-3-ol, 85267-91-0; isopropyllithium tetramethylethylenediamine complex, 85282-16-2; 1,2-diphenyl-4-methylpentan-1-one, 20736-42-9; 2,3-diphenyl-4-methyl-1-penten-3-ol, 85267-92-1; 1,2-diphenyl-3-methylcyclopropene, 51425-87-7; 1,2-diphenylcyclopene, 24168-52-3; 2-diazopropane, 2684-60-8.

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[75] We thank Professor Byron Rubin for the single X-ray structure determination of the endo-substituted 1,2-diazabicyclo[3.1.0]hex-2-ene 15. Details will be reported elsewhere.