Cycloaddition of Alkenylidenecyclopropanes with 4-Phenyl-1,2,4-triazoline-3,5-dione[1]

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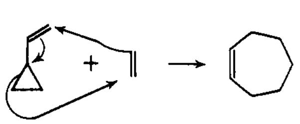
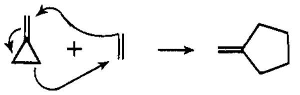
Abstract: Alkenylidenecyclopropanes **1** react rapidly with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) to form 6-isopropylidene-7-alkylidene-1,3,5-triazabicyclo[3.3.0]octane-2,4-diones (**2**). The stereochemistry about the 7-alkylidene functions in **2** has been established, and the observed stereochemical features of the reactions are discussed in terms of the Möbius–Hückel concept of orbital interactions occurring in the transition states for the reactions. The extremely facile cycloaddition and mode of reaction of **1** with PTAD are contrasted with the reactions of methylenecyclopropanes with PTAD. The differences in reactivity and mode of reaction are discussed in terms of a MO description of the bonding in **1** involving interaction between the C_4–C_5 π bond and the Walsh orbitals of the cyclopropane ring leading to a particularly favorable frontier orbital interaction in the transition states for cycloaddition which is not present in the methylenecyclopropanes or the transition states for reaction of the methylenecyclopropanes with PTAD. The 1:1 adducts **2** in most cases react further with PTAD to form 2:1 adducts. The structures and stereochemical features of these $({}_{\pi}4 + {}_{\pi}2)$ cycloaddition reactions are discussed in terms of the structural features present in the 1:1 adducts.

The $({}_{\pi}4 + {}_{\pi}2)$ cycloaddition of functionally substituted 1,3-alkadienes with alkenes (the Diels–Alder reaction) has provided the synthetic organic chemist with a powerful method for the synthesis of six-membered ring compounds.[2] The extremely facile nature of the $({}_{\pi}4 + {}_{\pi}2)$ cycloaddition reactions, compared with $({}_{\pi}2 + {}_{\pi}2)$ cycloaddition reactions of alkenes, has been discussed in terms of conservation of orbital symmetry[3a] and frontier orbital interactions[3b] in the respective transition states.

Cycloaddition reactions in which one of the π bonds of either the diene or the dienophile is replaced by a strained σ bond are less well known. A number of $({}_{\sigma}2 + {}_{\pi}2)$ cycloadditions involving the participation of a strained σ bond of a cyclopropane have recently been reported. Bicyclo[1.1.0]butanes[4] and bicyclo[2.1.0]pentanes[5] react with reactive dienophiles in $({}_{\sigma}2 + {}_{\pi}2)$ cycloaddition reactions *via* diradical intermediates. Cyclopropanones undergo numerous cycloaddition reactions in which the cyclopropanone ring suffers cleavage.[6]

Examples of the participation of a strained σ bond of a cyclopropane derivative in a (4 + 2) cycloaddition reaction are less well known. It is surprising that such reactions have not received attention previously, particularly in view of the synthetic potential such reactions might possess in the synthesis of five- and seven-membered ring systems (represented in a very naive fashion in eq 1 and 2). An example of the type of reaction illustrated in eq 1 has appeared, that being the reaction of α-cyclopropylstyrene with maleic anhydride to produce 4-phenylcyclohept-4-ene-1,2-dicarboxylic anhydride.[7-9]


(1)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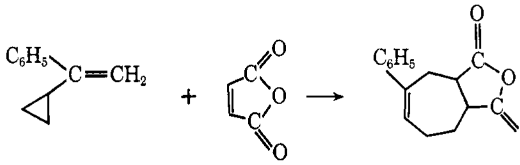

In view of the paucity of information on reactions of the type illustrated in eq 1 and 2, we initiated an investigation of cycloaddition reactions of cyclopropane-containing compounds. We have reported preliminary results on the reaction of alkenylidenecyclopropanes **1**[10] and methylenecyclopropanes[11] with 4-phenyl-1,2,4-

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(1) (a) Cycloaddition Reactions of Cyclopropane-Containing Systems. III. For the previous paper in this series, see D. J. Pasto and A. F.-T. Chen, *Tetrahedron Lett.*, 2995 (1972). (b) Submitted by A. F.-T. C. in partial fulfillment of the requirements of the Ph.D., University of Notre Dame, Notre Dame, Ind., 1972.

(2) A. Wasserman, "Diels–Alder Reactions," Elsevier, New York, N. Y., 1965; J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); **6**, 16 (1967).

(3) (a) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2047, 4388 (1965); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); (b) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 513.

(4) A. Cairncross and E. P. Blanchard, Jr., *J. Amer. Chem. Soc.*, **88**, 496 (1966); M. Pomerantz, G. W. Gruber, and R. N. Wilke, *ibid.*, **90**, 5040 (1968); C. D. Smith, *ibid.*, **88**, 4273 (1966).

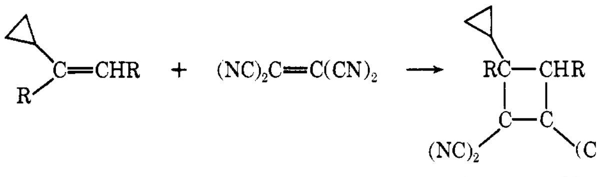
(5) P. G. Gassman and G. D. Richmond, *ibid.*, **92**, 2090 (1970); **90**, 5637 (1968); *Chem. Commun.*, 1630 (1968); P. G. Gassman and K. T. Mansfield, *J. Amer. Chem. Soc.*, **90**, 1524 (1968); *Chem. Commun.*, 391 (1965); P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Amer. Chem. Soc.*, **91**, 1684 (1969).

(6) N. J. Turro, S. S. Edelson, and R. B. Gagosian, *J. Org. Chem.*, **35**, 2058 (1970), and references cited therein.

(7) S. Sarel and E. Breuer, *J. Amer. Chem. Soc.*, **81**, 6522 (1959).

(8) We have been unable to reproduce this reaction under the reported reaction conditions. We are continuing to pursue investigations of this type of reaction.

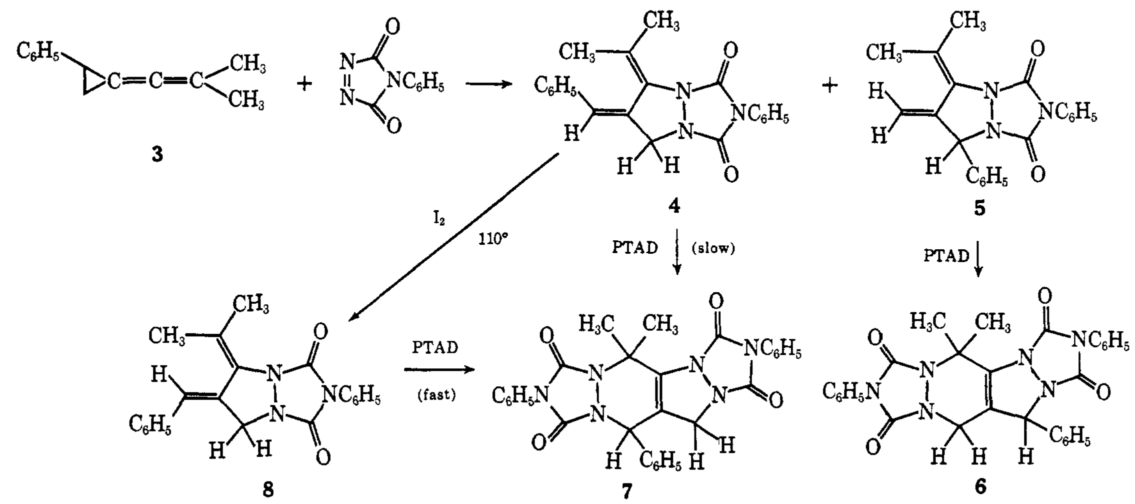
(9) More recently it has been reported that a number of vinylcyclopropanes react with tetracyanoethylene in $({}_{\pi}2 + {}_{\pi}2)$ cycloaddition reactions: F. Effenberger and W. Podszun, *Angew. Chem., Int. Ed. Engl.*, **8**, 976 (1969); S. Nishida, I. Moritani, and T. Teraji, *Chem. Commun.*, 501 (1970).

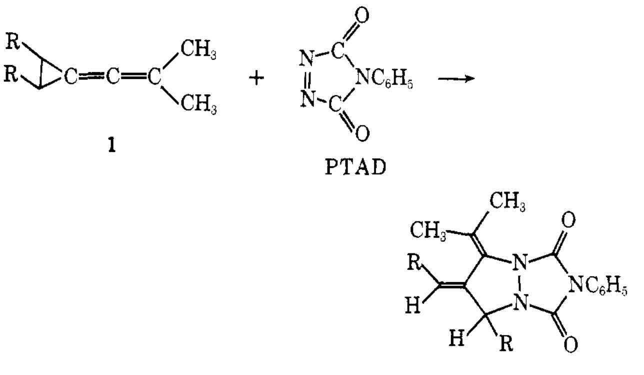


(10) D. J. Pasto and A. F.-T. Chen, *J. Amer. Chem. Soc.*, **93**, 2562 (1971).

(11) See reference in footnote 1.

Scheme I

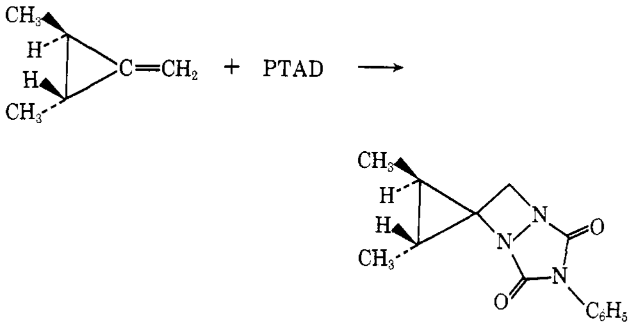




1 PTAD

2

triazoline-3,5-dione (PTAD).[12] Whereas alkenylidenecyclopropanes react very rapidly with PTAD to give products of general structure 2,[10] methylenecyclopropanes undergo only very slow (2 + 2) cycloaddition of the exocyclic double bond with PTAD.[11]



Results

2-Phenylisobutenylidenecyclopropane (3) with PTAD.

The addition of 1 equiv of a 0.4 *M* solution of PTAD in dichloromethane to 1 equiv of a 0.4 *M* solution of 3 in dichloromethane at 0° resulted in the immediate disappearance of the red color of the PTAD. Removal of the solvent and chromatographic separation of the residue on silica gel led to the isolation of unreacted 3, a mixture of the 1:1 adducts 4 and 5 (37.3 and 24.9%, respectively), and the 2:1 adduct 6 (9.3%). Fractional recrystallization of the 1:1 adduct mixture afforded pure fractions of 4 and 5 (see Scheme I).

The structures of the 1:1 adducts are assigned on the basis of chemical and spectral data. Ozonolysis of 0.095 mmol of 4 in 1.0 ml of dichloromethane and 0.2 ml of pyridine produced 0.090 mmol of benzaldehyde and 0.088 mmol of acetone (by glpc analysis) indicating the presence of a benzylidene and an isopropylidene function. The nmr spectrum is consistent with the gross structure represented in 4. The $-CH_2-$ of 4 appears as a doublet ($J = 1.3$ Hz) due to long-range coupling with the benzylidene vinyl hydrogen. The appearance of the $-CH_2-$ as the X_2 portion of an AX_2 system implies that the structure is planar about the bridgehead nitrogens and is consistent with previous observations that the urazol rings in adducts derived from PTAD are planar.[14,15]

The stereochemistry about the benzylidene function in 4 was indicated by the nmr spectrum which displays a very high-field methyl resonance at δ 1.37 for one of the methyls of the isopropylidene function. This high-field resonance is assigned to the methyl residing on the "inside" of the diene chromophore which suffers long-range shielding by the phenyl group. The phenyl group must be twisted perpendicular to the general plane of the diene system owing to severe steric interactions arising between the inside phenyl and methyl functions as required in a planar conformation. Confirmation of the stereochemical assignment was provided by the quantitative isomerization of 4 to 8 by iodine in benzene at 110° and by comparison of the spectral properties of 4 and 8. The high-field methyl resonance of 4 appears at much lower field in 8 (δ 2.13). The uv

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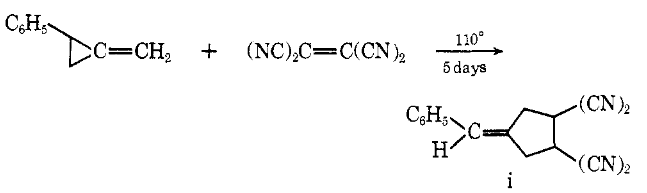
(12) Subsequent to the initiation of our studies it was reported that 2-phenyl- and 2,2-diphenylmethylenecyclopropane undergo concerted cycloaddition with tetracyanoethylene to form adducts of structure i.[13] These observations are in distinct contrast with our results derived



i

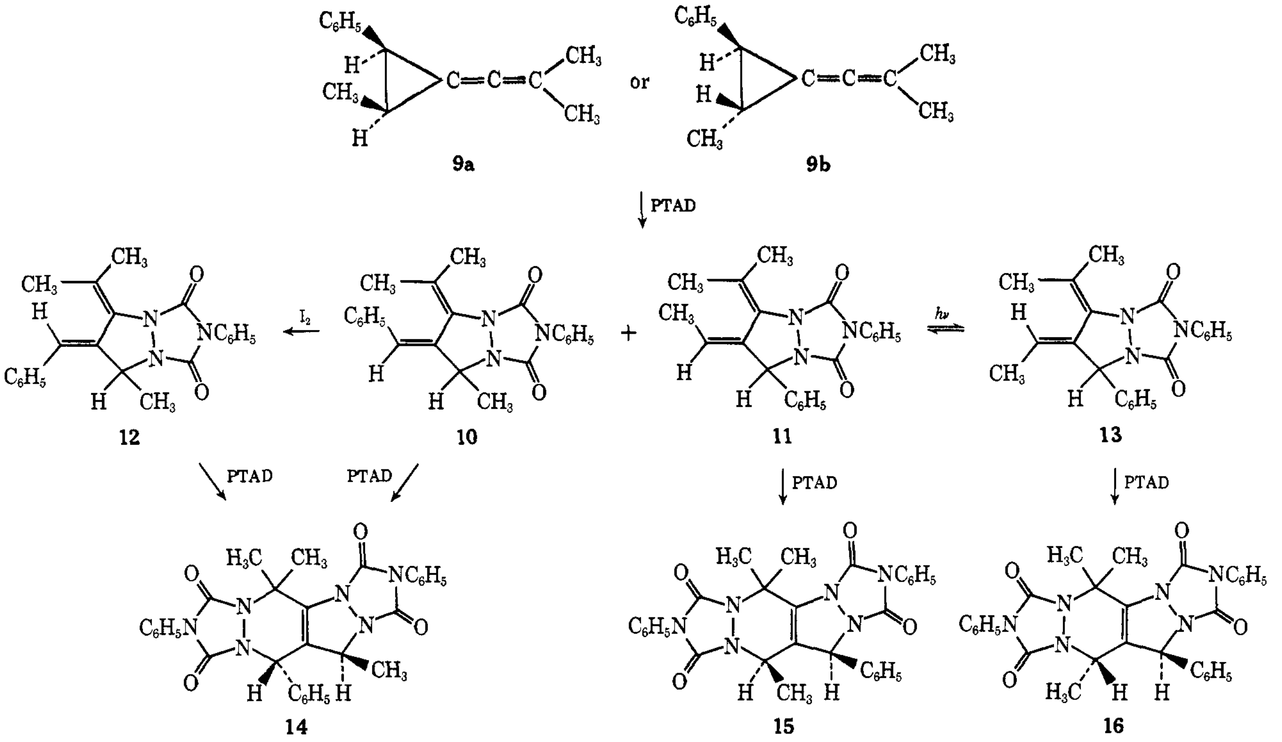
from reactions of methylenecyclopropanes with PTAD[11] and will be discussed in greater detail later in this paper.

(13) R. Noyori, N. Hayashi, and M. Kato, *J. Amer. Chem. Soc.*, **93**, 4948 (1971).

(14) A. B. Evnin, D. R. Arnold, L. A. Karnishky, and E. Strom, *ibid.*, **92**, 6218 (1970).

(15) *cis*- and *trans*-piperylene react with PTAD to give identical adducts which is consistent with a planar structure about the nitrogen atoms. The nmr spectra of the adducts of *cis*- or *trans*-piperylene with PTAD determined at various temperatures are not consistent with a rapidly interconverting set of nonplanar structures.

Scheme II



absorption maximum of **8** appears at significantly longer wavelength (274 nm relative to 268 nm with **4**) consistent with more extensive conjugation in **8** in which the phenylbutadiene system is capable of existing in a planar conformation.

The structure of **5** was immediately indicated by its nmr spectrum which contained resonances characteristic of isopropylidene and methylene functions. Further support for the proposed structure was provided by quantitative ozonolysis which produced 0.94 molar equiv of acetone but no benzaldehyde.

The structures of the 2:1 adducts **6** and **7** were assigned by comparison with the 2:1 adducts derived by further reaction of **4**, **5**, and **8** with PTAD. The 2:1 adduct derived from the reaction of **3** with PTAD is identical with the adduct derived by reaction of **5** with PTAD. The 1:1 adducts **4** and **8** reacted with PTAD to give the same 2:1 adduct **7**; however, **8** reacted considerably faster than did **4**.

***cis*- and *trans*-2-Methyl-3-phenylisobutenylidenecyclopropane (9a and 9b) with PTAD.** Treatment of *cis*- and *trans*-2-methyl-3-phenylisobutenylidenecyclopropane with PTAD produces nearly identical mixtures of the 1:1 adducts **10** and **11**. The structure and stereochemistry of **10** were clearly evident from the nmr spectrum which contained a high-field methyl resonance (δ 1.39) and by iodine-catalyzed isomerization to **12**. Both **10** and **12** react further with PTAD to produce, surprisingly, identical 2:1 adducts (**14**) (Scheme II). Apparently the conformations of **10** and **12** are substantially different such that PTAD approaches opposite sides of the diene system in the molecules. The stereochemical relationship of the phenyl and methyl functions in **14** is assigned trans based on comparison of the chemical shifts of the methyl functions in **14**, **15**, and **16**. The methyl resonances in **14** and **16** appear at considerably lower field (δ 1.66 and 1.47, respectively) than in **15** (δ 0.75). Inspection of molecular models indicates that in the cis isomer **15**, the phenyl and methyl reside in nearly the same plane (the tetracyclic framework of the 2:1 adducts is nearly planar), and that the steric interaction between the proximate phenyl and methyl forces the phenyl into a twisted conformation perpendicular to the general plane of the molecule such that the methyl resides over the face of the phenyl ring. Such is not indicated to occur in the trans structures **14** and **16**.

Assignment of structure **11** for the other 1:1 adduct is based on a comparison of its nmr spectrum with that of **13**. The isomerization of **11** to **13** could not be achieved by refluxing with iodine in benzene. Irradiation of **11** in the presence of benzophenone in benzene afforded an inseparable 70:30 mixture of **13** and **11**. Unfortunately, this product distribution does not represent a true ground-state thermodynamic equilibrium and thus cannot be used to assign structures on that basis. The ethylidene vinyl hydrogen of **13**, however, appears at lower field than in **11** owing to long-range shielding by the isopropylidene function.[16]

In contrast to the reactions of **10** and **12** with PTAD which gave identical 2:1 adducts, the stereoisomeric adducts **11** and **13** reacted with PTAD to produce different 2:1 adducts. The stereochemical relationship between the methyl and phenyl is assigned cis and trans in **15** and **16**, respectively, based on the long-range shielding of the phenyl on the methyl resonance (*vide infra*) and consideration of the stereochemistry of $({}_{\pi}4 + {}_{\pi}2)$ cycloadditions in which the PTAD approaches the diene chromophore from the side opposite the phenyl group.

***cis*- and *trans*-2,3-Dimethylisobutenylidenecyclopropane (17a and 17b) with PTAD.** The reactions of **17a** and **17b** with PTAD produced only a single 1:1 adduct

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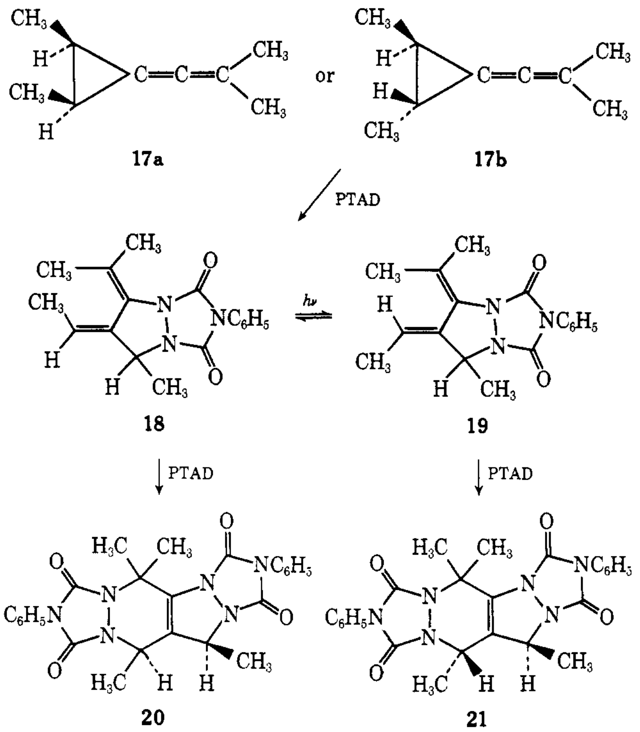
(16) This trend is noted not only with all of the PTAD adducts described in this article, but also with the adducts formed with CSI which are reported elsewhere.[17]

(17) D. J. Pasto, A. F.-T. Chen, G. Ciurdaru, and L. A. Paquette, *J. Org. Chem.*, in press.

18. The assignment of the stereochemistry about the ethylidene function is based on a comparison of the chemical shifts of the ethylidene vinyl hydrogens of **18** and **19**, the latter obtained by benzophenone-sensitized photoisomerization of **18**, the vinyl hydrogen resonance of **19** appearing at δ 5.77 compared to δ 5.59 in **18**.

Adduct **18** slowly reacts further with PTAD to give a 2:1 adduct assigned structure **20** (see Scheme III).

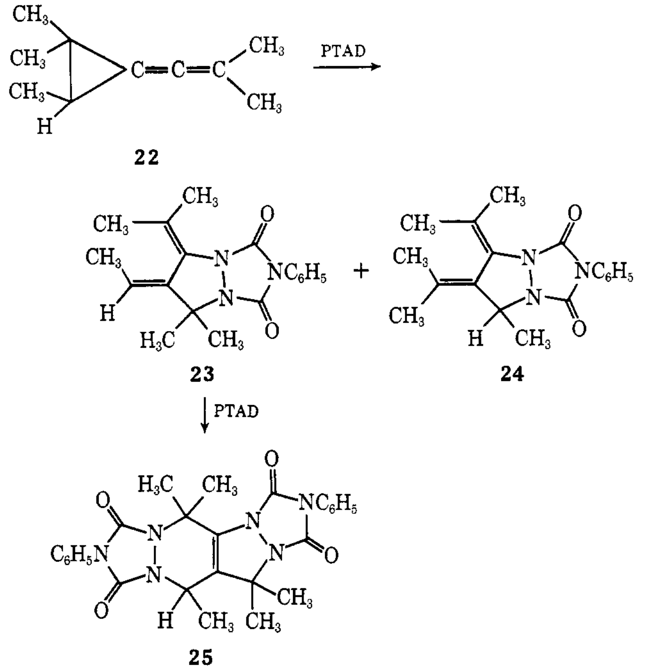
Scheme III



The assignment of the stereochemistry of **20** is based on the assumption that PTAD approaches **18** from the side opposite the methyl attached to the sp^3 carbon resulting in a cis relationship between the two methyls in **20**. The nmr spectrum of **20** is also consistent with this assignment. The doublet representing the methyl attached to the six-membered ring of **20** appears at the same position as in the 2:1 adduct **25** in which the methyl must be cis to one of the methyls attached to the five-membered ring.

2,2,3-Trimethylisobutenylidenecyclopropane (22) with PTAD. The reaction of **22** with PTAD produces a 65:35 mixture of the 1:1 adducts **23** and **24** (by nmr analysis). Fractional recrystallization of the mixture gave a pure fraction of **23**; however, **24** could not be obtained in pure form using physical separation techniques. The structure of **23** was assigned on the basis of chemical and nmr spectral properties. Quantitative ozonolysis of **23** produced acetaldehyde and acetone indicating the presence of ethylidene and isopropylidene functions. The stereochemistry about the ethylidene function was assigned by comparison of the chemical shift of the ethylidene vinyl hydrogen of **23** (δ 5.55) with that in **18** (δ 5.59). The chemical shift of the ethylidene methyl function in the two compounds is also very similar (δ 1.70 in **23** compared to δ 1.73 in **18**). Attempted benzophenone-sensitized photoisomerization of **23** met with failure. Further reaction of **23** with PTAD led to the formation of **25** (see Scheme IV).

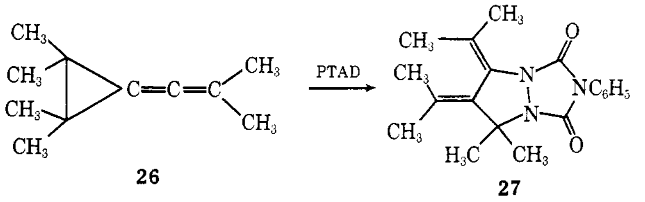
Scheme IV



Treatment of the mixture of **23** and **24** with PTAD indicated that **23** rapidly reacts with PTAD but that **24** reacts only very slowly (the product does not appear to be a (4 + 2) cycloaddition product). Reaction of **23** in the mixture of **23** and **24** followed by chromatographic separation of the 2:1 adduct **25** from **24** led to the isolation of pure **24**. The lack of reactivity of **24** with PTAD is consistent with the observed lack of reactivity of **27** with PTAD (*vide infra*).

2,2,3,3-Tetramethylisobutenylidenecyclopropane (26) with PTAD. Alkenylidenecyclopropane **26** reacts somewhat more slowly with PTAD to produce **27** (Scheme V). The structure of **26** is indicated by the nmr spectrum which displays singlets at δ 1.76 (12 H), 1.87 (3 H), and 2.13 (3 H), with the aromatic hydrogens appearing as a multiplet at δ 7.35. Adduct **27** reacts very slowly with PTAD but not to form a (4 + 2) cycloaddition product.

Scheme V



Discussion

A careful inspection of the results presented in the foregoing section reveals two interesting and important stereochemical facts. The reactions of 2-phenyl- (**3**) and the cis- and trans-2,3-disubstituted isobutenylidenecyclopropanes, **9a** and **9b**, and **17a** and **17b** with PTAD produced 1:1 adducts which possess only the less thermodynamically stable *Z* stereochemistry about the 7-alkylidene functions. Secondly, both the *cis*- and *trans*-2-methyl-3-phenyl- (**9a** and **9b**) and the *cis*- and *trans*-2,3-dimethylisobutenylidenecyclopropanes (**17a** and **17b**) reacted to give identical 1:1 adducts. Based on these data, we previously suggested that the reactions of **1** with PTAD proceed *via* concerted re-

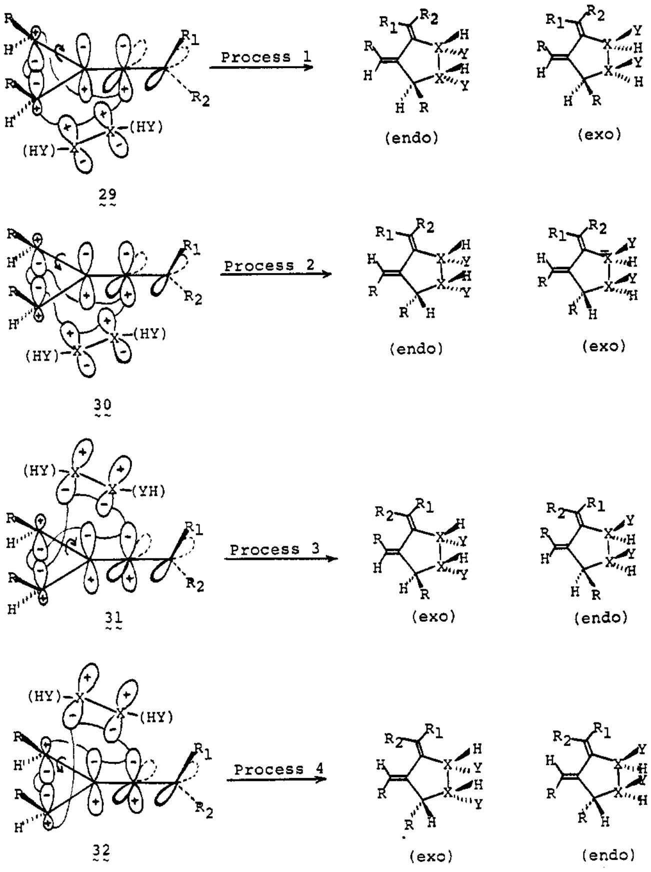


Figure 1. "Six-electron" transition states for cycloaddition reactions of alkenylidene- and methylenecyclopropanes.

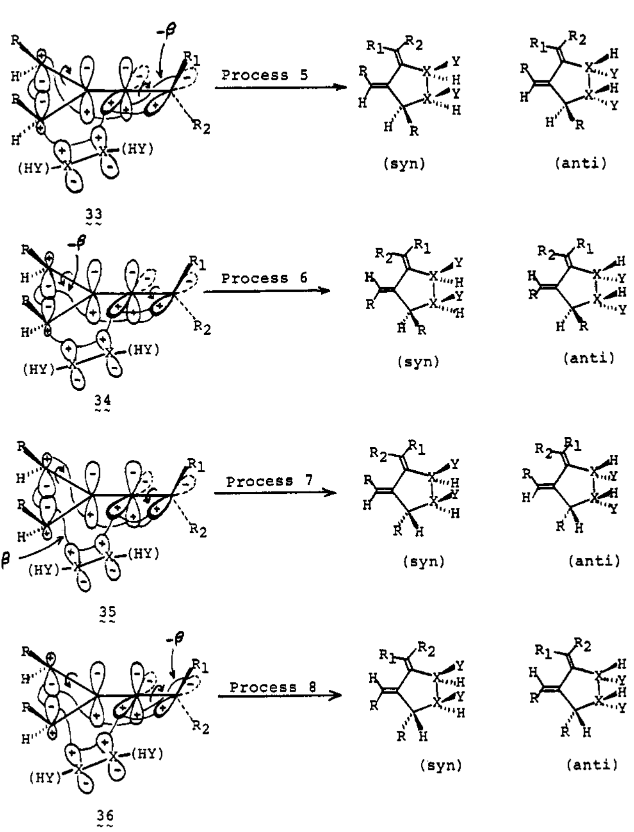
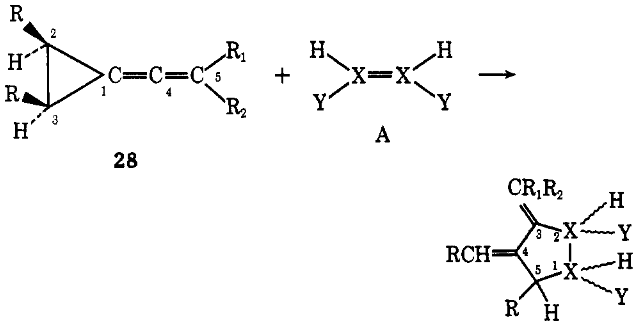


Figure 2. "Eight-electron" processes for the cycloaddition reactions of alkenylidenecyclopropanes.

action pathways[10] in which the stereochemistry about the 7-alkylidene function is governed by orbital overlap developed in the transition states for the cycloaddition reactions.[11,18] We now wish to present a more detailed description of the stereochemical aspects of these reactions, as well as the ground and transition state orbital interactions of **1** in reaction with PTAD which afford a high degree of reactivity of **1** with PTAD relative to methylenecyclopropanes.

The concerted cycloaddition of an alkenylidenecyclopropane with a dienophile can occur *via* two distinctly different modes of reaction. One mode involves interaction of the dienophile with the π electrons of the C_1–C_4 double bond and the σ electrons of the strained C_2–C_3 bond (designated as a "six-electron" process). The second mode of reaction involves the π electrons of both the C_1–C_4 and C_4–C_5 double bonds and the σ electrons of the strained C_2–C_3 bond (designated as an "eight-electron" process). For the reaction of the alkenylidenecyclopropane **28** with the hypothetical dienophile A, there are four stereochemically different processes for each mode of reaction (illustrated in Figures 1 and 2). These stereochemically different processes produce different combinations of stereochemical features at (1) the 3-alkylidene function, (2) the 4-alkylidene function, (3) at C_5, and (4) at the X atoms relative to C_5.



Four stereochemically different, thermally allowed

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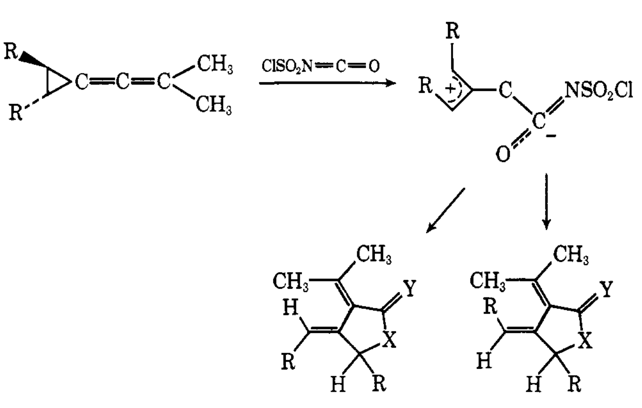
(18) Alternate pathways proceeding *via* dipolar or diradical intermediates are not considered likely based on the following considerations. Reactions of the trans-2,3-disubstituted alkenylidenecyclopropanes with chlorosulfonylisocyanate produce cyclopropane ring-opened intermediates which collapse to produce a mixture of adducts



Y = NSO_2Cl; X = O
Y = O; X = NSO_2Cl

stereoisomeric about the alkylidene function.[17] The reaction of **9b** or **17b** with PTAD *via* dipolar intermediate mechanisms would similarly be expected to produce mixtures of **10**, **12**, **11**, and **13**, and **18** and **19**, respectively. Reactions involving the formation of diradical intermediates, either cyclopropyl or cyclopropylcarbinyl, are not expected to lead to cyclopropane ring-opened products.

concerted "six-electron" processes are possible, *i.e.*, those proceeding *via* aromatic Hückel transition states.[19] In the representations of these transition states in Figure 1 the interacting orbitals in the transition states are connected by lines to aid in visualizing the various processes. (The nonthermally allowed concerted, antiaromatic transition state processes are not shown).

Approach of the dienophile to the side of **28** opposite the R functions at C_2 and C_3 in an "endo" configuration (the Y functions of the dienophile being directed toward **28**) with inversion occurring at C_3 produces transition state **29** giving the (endo) product (process 1).[21] Reaction *via* an "exo" configuration (Y functions directed away from **28**) results in the formation of a product stereoisomeric at X_1 and X_2 [the (exo) product in process 1].[22] In these transition states the stereochemistry about the C_3 alkylidene function is determined solely by the direction of approach of the dienophile, in this process R_2 becomes syn to X_2. The direction of rotation of the plane of the H–C_2–R moiety is dictated by the requirement for an "aromatic" transition state and results in the formation of the *Z* isomer.

In process 2, the dienophile again approaches the side of **28** opposite the R functions; in this process, however, retention of stereochemistry at C_3 is pictured as occurring giving the (endo and exo) products *via* transition state **30**. Processes 3 and 4 picture transition states derived by the approach of the dienophile cis to the R functions.

A more careful consideration of the steric requirements for orbital overlap in transition states **29–32** immediately indicates that none of these processes should be particularly favorable. The C_4 p orbital of the C_1–C_4 double bond is orthogonal to the plane of the cyclopropane ring and the axis of the C_2–C_3 bond which is being broken. In the C_3 inversion processes the p orbitals of the dienophile must span the orthogonal C_4 p orbital and the orbital on C_3, a feat which does not allow for effective orbital overlap early along the reaction coordinate. Similarly, overlap between the orbitals on C_2 with the C_1 p orbital cannot occur until considerable rotation of the H–C_2–R plane has occurred.

The initial orbital overlap derived in the retention processes appears even less favorable, the π system of the dienophile having to penetrate past the C_1 p orbital.

The stereochemical processes of the "eight-electron" mode of reaction are illustrated in Figure 2.[19] In the C_3 inversion processes the dienophile approaches the "edge" of the alkenylidenecyclopropane with the Y functions of the dienophile either "syn" or "anti" with respect to the R groups attached to C_2 and C_3.[22] In these processes the p orbitals of the dienophile can readily initiate bonding with the p orbital on C_4 of the C_4–C_5 double bond and the orbital on C_3, all of the orbitals residing in a common plane. In contrast, it is not possible to initiate bonding between the dienophile and the requisite orbitals of the alkenylidenecyclopropane in the retention processes 7 and 8. Comparison of the steric requirements in the "six-" and "eight-electron" inversion processes leads one to the prediction that the "eight-electron" mode of reaction should be more favorable. We will return to this point later in this article.

In the "eight-electron" mode of reaction the direction of rotation of the $=CR_1R_2$ function is not dependent on the direction of approach of the dienophile to the alkenylidenecyclopropane but is intimately connected with the stereochemistry of attack at C_3 and the direction of rotation of the plane of the H–C_2–R moiety. Of the two inversion processes, process 5 is expected to be favored over process 6 in early transition states owing to the steric interference to inward rotation of H–C_2–R generated between R and the cis group on C_3. In contrast, process 6 is expected to be more favorable if the transition state occurs late along the reaction coordinate due to the very severe steric interference between R and R_1, both of which reside on the "inside" of the diene chromophore; the observations that in general the reactions of the alkenylidenecyclopropanes occur very rapidly, and only adducts containing the *Z* stereochemistry about the 7-alkylidene are formed, indicate that the cycloaddition reactions occur *via* the inversion process 5.[24]

In the foregoing discussion, we have centered our attention only on the stereochemical aspects of the reaction with a cis-2,3-disubstituted alkenylidenecyclopropane. In cycloaddition reactions involving trans-2,3-disubstituted alkenylidenecyclopropanes, the R in the H–C_2–R plane will rotate outward (the direction of least steric interference) to produce the (*Z*)-7-alkylidene function. Attack at C_3 is still favored to occur with inversion (process 5). Thus, the only difference between reactions of the cis and trans compounds will be the stereochemistry at C_8 in the 1:1 adducts.

The foregoing approach provides an excellent basis for the discussion of the stereochemical aspects of the cycloaddition reactions; it does not, however, provide a completely satisfactory rationale for the high degree of reactivity of the alkenylidenecyclopropanes with PTAD or the differences in reactivity and mode of reaction between alkenylidene- and methylenecyclopropanes with PTAD. The differences in reactivity and mode of reaction become more apparent using an alternate MO description of bonding in the alkenyli-

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[19] Aromatic Hückel transition states are those containing $(4n + 2)$ electrons and zero, or an even number, of antibonding interactions ($-\beta$'s). Transition states containing $4n$ electrons are considered aromatic (thermally allowed) when an odd number of $-\beta$'s (Möbius systems) are present.[20]

[20] H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971).

[21] In all of the processes illustrated in Figures 1 and 2, the addition across the π-electron system of the dienophile is depicted as occurring in a suprafacial manner. Antarafacial additions are in general less favorable than suprafacial additions owing to the more stringent steric demands in the antarafacial transition states.

[22] In the reactions of alkenylidenecyclopropanes with PTAD stereoisomerism about the bridge nitrogens in the adducts is not present due to the planar structure of the urazole ring,[14] and, unfortunately, no information is thus available concerning the "endo–exo" or "syn–anti" (*vide infra*) nature of the transition states. Attempted reactions of alkenylidenecyclopropanes with dienophiles capable of producing adducts possessing stereochemistry at the bridgehead positions (*e.g.*, maleic anhydride) were unsuccessful. Attempted reactions at temperatures >150° resulted in isomerization of the alkenylidenecyclopropanes to bismethylenecyclopropanes[23] thus precluding the use of high-temperature reaction conditions.

[23] M. E. Hendrick, J. A. Hardie, and M. Jones, Jr., *J. Org. Chem.*, **36**, 3061 (1971); D. R. Paulson, J. K. Crandall, and C. A. Bunnell, *ibid.*, **35**, 3708 (1970); R. Bloch, P. LePerchec, and J.-M. Conia, *Angew. Chem.*, **82**, 910 (1970).

[24] The results reported in this article provide stereochemical information involved in the formation of the 7-alkylidene function. Studies directed toward determination of the stereochemistry of reaction at C_3 and the direction of rotation of the $=CR_1R_2$ function have been initiated.

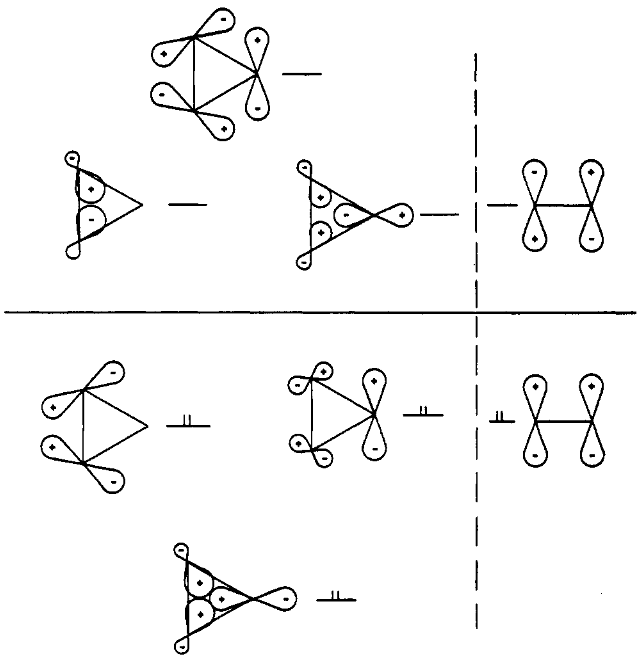

Figure 3. Walsh and π orbitals of an alkenylidenecyclopropane.

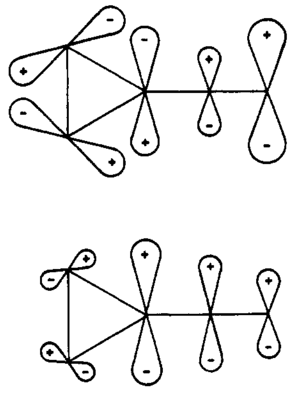

Figure 4. "π-Type" MO's of an alkenylidenecyclopropane.

dene- and methylenecyclopropanes and in the transition states for cycloaddition. This MO description of an alkenylidenecyclopropane invokes an interaction between the C_4–C_5 π system and the orbitals of the cyclopropane ring. In this approach it is convenient to use the MO description of cyclopropane proposed by Walsh in which the carbon atoms are considered to be sp^2p hybridized.[25] The hydrogens are bonded to two of the sp^2 hybrid orbitals, the third sp^2 orbital of each carbon being directed toward the center of the three-membered ring forming the lowest energy "Walsh" orbital. The remaining p orbitals combine to form a degenerate pair of orbitals, the maximum overlap of which occurs "outside" the internuclear axes.

Application of the Walsh model to alkenylidene- and methylenecyclopropanes requires a slight modification, C_1 now being sppp hybridized. The "Walsh" orbitals of the three-membered ring in the alkenylidene- and methylenecyclopropanes are constructed as illustrated in the left-hand portion of Figure 3.[26] Interaction of the antisymmetric component of the originally degenerate pair of bonding orbitals with the C_4–C_5 π^* in an alkenylidenecyclopropane,[27] and the originally nondegenerate unoccupied orbital with the C_4–C_5 π MO, produces two new "π-type" MO's embracing the C_4–C_5 double bond and the cyclopropane ring system as illustrated in Figure 4. The highest occupied "combined Walsh" orbital of the alkenylidenecyclopropane possesses the correct symmetry for interaction with the unoccupied orbital of the dienophile (π^* in Figure 5) in a concerted cycloaddition reaction. Furthermore, the substantial antibonding character between C_2 and C_3 in the highest occupied Walsh orbital of the alkenylidenecyclopropane participating in the frontier orbital should greatly facilitate cleavage of the C_2–C_3 bond in the transition state.

The qualitative MO description developed in the foregoing paragraphs is quantitatively borne out by the results of extended Hückel (EH) calculations employing nonorthogonal basis sets.[30] The highest occupied orbitals of cyclopropane are a set of degenerate orbitals of A_1 and B_1 symmetry which correspond to the symmetric and antisymmetric Walsh bonding orbitals (see Figure 5). The B_1 orbital of cyclopropane correlates with the two B_1 orbitals of alkenylidenecyclopropane (Figure 5) which correspond to those developed in the qualitative approach developed earlier in this article. The highest energy B_1 orbital is the highest occupied orbital of alkenylidenecyclopropane and has the appropriate symmetry for interaction with the dienophile (*vide infra*). In contrast, the A_1 Walsh orbital of cyclopropane is not affected by the introduction of the sppp hybridized C_1 and the C_4–C_5 π system as evidenced by inconsequential changes in coefficients and energy in going from the A_1 orbital of cyclopropane to the corresponding A_1 orbital of the alkenylidenecyclopropane.

The EH calculations provide a number of additional interesting insights worthy of mention. First, in the

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(25) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); *Nature (London)*, **159**, 167, 712 (1947).

(26) The replacement of a sp^2p hybridized carbon by a sppp hybridized carbon is expected to result in a destruction of the degeneracy of the degenerate pairs of "Walsh" orbitals in cyclopropane (confirmed by extended Hückel calculations for methylenecyclopropane); however, the loss of the degeneracy of the Walsh orbitals will not affect the qualitative conclusions drawn from this approach.

(27) The π MO of the C_4-C_5 π system is placed approximately at the same energy level as the degenerate pair of occupied Walsh orbitals based on a comparison of the photoelectron ionization potentials of cyclopropane (10.53 eV)[28] and ethylene (10.48 eV).[29] Again, the replacement of sp^2p hybridized carbon by sppp hybridized carbon will alter the ionization potentials but the qualitative conclusions derived will not be substantially effected.

(28) H. Basch, M. B. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.*, **51**, 52 (1969).

(29) M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964).

(30) The following bond angles and lengths were employed in the calculations. Cyclopropane: C-H bond length, 1.010 Å; C-C bond length, 1.524 Å; H-C-H bond angle, 120°. Methylenecyclopropane: C_2-H bond length, 1.010 Å; C_1-C_2, C_2-C_3, and C_3-C_1 bond lengths, 1.524 Å; C_1-C_4 bond length, 1.309 Å; C_4-H bond lengths, 1.061 Å; H-C_2-H bond angle, 120°, H-C_4-H bond angle, 120°. Alkenylidenecyclopropane: C_4-C_5 bond length, 1.309 Å; C_5-H bond lengths, 1.061 Å; H-C_5-H bond angle, 120°; the remainder of bond lengths and bond angles are the same as in methylenecyclopropane.

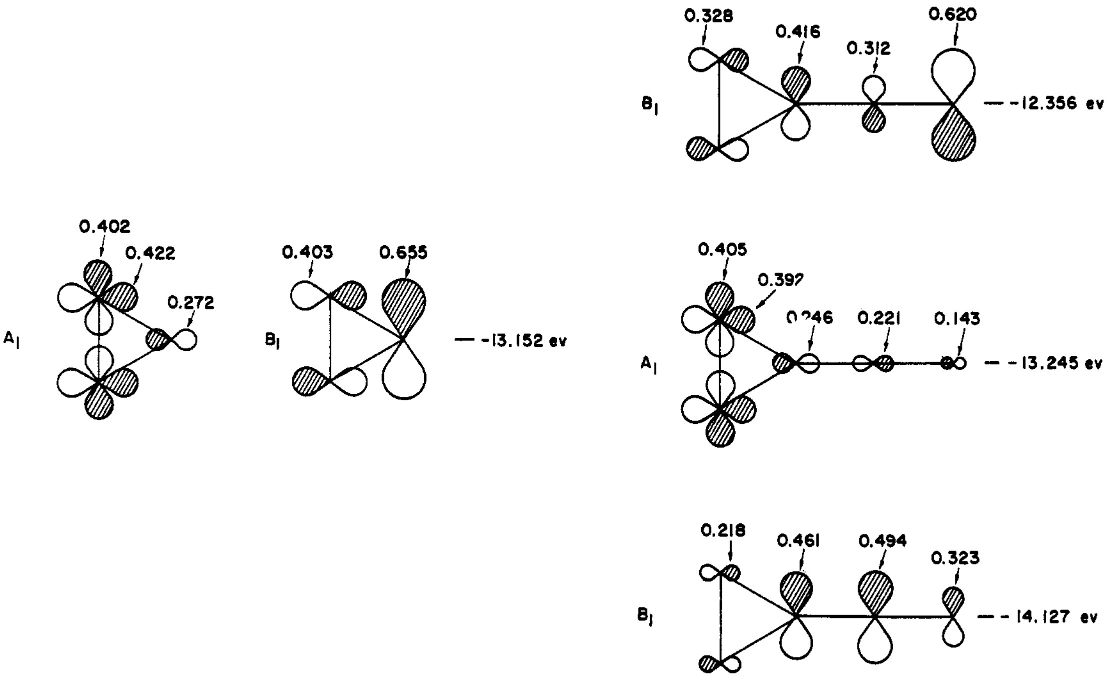

Figure 5. Results of EH calculations for cyclopropane and ethenylidenecyclopropane.

alkenylidenecyclopropane considerable electron density has shifted from the cyclopropane moiety to the C_4–C_5 π system. This is consistent with the observed greater inductive donation afforded by cyclopropane relative to a double bond as manifest in the greater rate of solvolysis of cyclopropylcarbinyl relative to allyl derivatives[31] and the high preference for electrophilic attack at C_4 and C_5 relative to C_1 in alkenylidenecyclopropanes.[32] Second, the antibonding character between C_2 and C_3 in the two B_1 Walsh-type orbitals of alkenylidenecyclopropane is considerably less than in the B_1 Walsh orbital of cyclopropane. This should be reflected in a strengthening (shortening) of the C_2–C_3 bond in alkenylidenecyclopropane relative to a C–C bond length in cyclopropane.[33,34]

A similar approach to the MO description for the cycloaddition of methylenecyclopropane immediately reveals that there does not exist suitable methylenecyclopropane MO's for interaction with a dienophile in the transition state. This is completely consistent with the tremendously lower reactivity and different mode of reaction of *cis*- and *trans*-2,3-dimethylmethylenecyclopropane with PTAD.

Formation of the 2:1 Adducts. The rates of reactions of the 1:1 adducts with PTAD to form the 2:1 adducts were observed to be quite sensitive to the degree of substitution at the 7-alkylidene function and to the stereochemistry about the 7-alkylidene double bond. The reactivity of the 1:1 adducts markedly decreases with increasing substitution at the 7-alkylidene function, the 7-isopropylidene derivatives **34** and **27** not undergoing reaction with PTAD despite the extremely reactive nature of PTAD. The reactivity of the *E* isomers **8**, **12**, **13**, and **19** was significantly greater (up to a factor of 10^2) than of the corresponding *Z* isomers **4**, **10**, **11**, and **18**. Furthermore, an interesting contrast is encountered in the reactions of the stereoisomeric 1:1 adducts **10** and **12**, which react with PTAD to produce the *same* 2:1 adduct, compared to the stereoisomeric adducts **11** and **13**, and **18** and **19**, each of which produces a unique 2:1 adduct.

These observations are readily rationalized if one considers the distortion of the diene chromophore that results when substituents are forced to reside in the "inside" of the diene system. The extreme steric crowding of functions constrained to the "inside" of the diene chromophore is reflected in the quantitative isomerizations of the *Z* isomers **4** and **10** to the *E* isomers **8** and **12**, respectively. The steric repulsion between the "inside" groups forces a twisting of the 6-isopropylidene and (*Z*)-7-alkylidene functions such that the conjugative interaction between the double bonds is reduced, as well as forcing the groups attached to the terminal carbons of the diene into sterically prominent positions above and below the diene chromophore. Both of these effects result in a reduction in the rate of cycloaddition with PTAD.

In the cycloaddition reactions of **11** and **13**, the PTAD approaches the diene from the side opposite the phenyl group attached to C_8 to produce the 2:1 adducts **15** and **16**, respectively. The assignment of the stereochemistry of **15** and **16** rests on the observed long-range shielding of the methyl group cis to the phenyl in **15** (*vide infra*). The reactions of **18** and **19** with PTAD are also consistent with attack by PTAD at the side opposite the C_8 methyl, although here the nmr evidence is not as definitive in support of the assigned stereochemistry as in the case of **15** and **16**.

The reactions of **10** and **12** with PTAD, however,

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(31) For a leading reference, see H. Hart and P. A. Law, *J. Amer. Chem. Soc.*, **86**, 1957 (1964).

(32) See ref 17.

(33) See R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); H. Gunther, *ibid.*, 5173 (1970).

(34) This MO description of the interaction of the C_4–C_5 double bond of an alkenylidenecyclopropane with the three-membered ring can be easily extended to other cyclopropane-containing systems. In particular, the high reactivity of bromomethylenecyclopropane toward solvolysis compared to vinyl bromide[35] and the mode of reaction of variously substituted alkenylidenecyclopropanes with chlorosulfonyl isocyanate[32] can be rationalized in terms of stabilization of the vacant orbital on C_4 by the Walsh orbitals of the cyclopropane ring.

(35) T. Bassler and M. Hanack, *Tetrahedron Lett.*, 2171 (1971).

both produce the same 2:1 adduct **14**. The assignment of the trans relationship between the methyl and phenyl in **14** appears to be soundly based. The reaction of **10** to produce **14** must occur by attack of PTAD on the same side of the diene chromophore as the C_8 methyl. The benzylidene function must be twisted below the plane of the diene relative to the C_8 methyl such that the phenyl group offers more steric resistance to attack by the PTAD than does the C_8 methyl. In **12** the benzylidene function is able to assume a planar conformation relative to the diene, the C_8 methyl now offering the greater steric inhibition to attack by PTAD on the diene chromophore as observed with the other 1:1 adducts.

Experimental Section

Preparation of Substituted Alkenylidenecyclopropanes. The procedure of Hartzler[36] was used to prepare the substituted alkenylidenecyclopropanes by addition of 3,3-dimethylallenecarbene to the appropriate alkenes. Alkenylidenecyclopropanes not previously reported are the following.

***cis*-2-Methyl-3-phenylisobutenylidenecyclopropane (9a):** bp 80–81° (0.03 mm); ir (capillary film) 2035 cm^{-1} (allene); nmr (CCl_4) δ 0.91 (d, $J = 6.0$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.80 (s, 3 H, $-CH_3$), 1.89 (s, 3 H, CH_3), 2.0 (dq, $J = 6.0$ and 9.0 Hz, 1 H, $>\mathrm{C}H\mathrm{CH}_3$), 3.08 (d, $J = 9.0$ Hz, 1 H, $>\mathrm{C}H(\mathrm{C_6H_5})$), and 7.17 (s, 5 H, aromatic H).

***trans*-2-Methyl-3-phenylisobutenylidenecyclopropane (9b):** bp 73–75° (0.03 mm); ir (capillary film) 2030 cm^{-1} (allene); nmr (CCl_4) δ 1.34 (d, $J = 5.0$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.71 (m, 1 H, $>\mathrm{C}H\mathrm{CH}_3$), 1.77 (s, 6 H, $=\mathrm{C(CH_3)_2}$), 2.41 (d, $J = 4.5$ Hz, 1 H, $>\mathrm{C}H(\mathrm{C_6H_5})$), and 7.10 (s, 5 H, aromatic H).

4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD). 4-Phenyl-1,2,4-triazolidine-3,5-dione[37] (17.5 g) was dissolved in 60 ml of dichloromethane and cooled to −70° in a Dry Ice–acetone bath and 12.1 g of freshly prepared *tert*-butyl hypochlorite was added over the course of 30 min. The reaction mixture was allowed to warm to room temperature and the majority of the solvent was removed under vacuum. The residue was filtered and washed with two 20-ml portions of cold dichloromethane. The PTAD was sublimed under vacuum prior to use.

Reaction of Substituted Alkenylidenecyclopropanes with PTAD. To a solution of the alkenylidenecyclopropane in dichloromethane (0.4 *M*) at 0° was added 1 molar equiv of PTAD in dichloromethane (0.4 *M*). After discharge of the red color of the PTAD, the solvent was removed under reduced pressure and the product mixture was separated by column chromatography on silica gel and/or fractional crystallization. The 1:1 adducts elute with 2:1 benzene–methylene chloride while the 2:1 adducts elute with chloroform. (Identical procedures were employed in the reactions of the 1:1 adducts with PTAD.)

Ozonolysis of Adducts. A weighed portion of the 1 : 1 adduct (~0.1 mmol) was dissolved in 1.0 ml of dichloromethane and 0.2 ml of pyridine. The solution was placed in a small bubbler tube, cooled to −70° in a Dry Ice–acetone bath, and was treated with ozone until no further consumption of ozone was indicated by use of a potassium iodide–starch indicator solution. The ozonolysis reaction mixture was allowed to warm to room temperature. A weighed portion of toluene was added (as an internal standard for glpc analysis) and the mixture was analyzed directly by glpc on a 10-ft Carbowax 20M on Chromosorb P column.

2-Phenylisobutenylidenecyclopropane (3) with PTAD. Adduct 4: mp 174.0–174.5° (ether); uv max (95% ethanol) 222 nm (log ϵ 4.31) and 268 (3.97); nmr ($CDCl_3$) δ 1.37 (s, 3 H, "inside" $\mathrm{C}H_3$ of $=\mathrm{C(CH_3)_2}$), 2.10 (s, 3 H, "outside" $\mathrm{C}H_3$ of $=\mathrm{C(CH_3)_2}$), 4.42 (d, $J = 1.3$ Hz, 2 H, CH_2), 6.53 (br s, 1 H, $=\mathrm{C}H(\mathrm{C_6H_5})$), and 7.40 (m, 10 H, aromatic H); mass spectrum *m/e* calcd for $C_{21}H_{19}N_3O_2$ 345.148, found 345.151.

Adduct 5: mp 126.0–126.5° (ether); uv max (95% ethanol) 222 nm (log ϵ 4.31) and 265 (3.21); nmr ($CDCl_3$) δ 1.99 (s, 3 H, "inside" $\mathrm{C}H_3$ of $=\mathrm{C(CH_3)_2}$), 2.20 (s, 3 H, "outside" $-CH_3$ of $=\mathrm{C(CH_3)_2}$), 5.31, 5.43, 5.65 (br s, 1 H each, vinyl H and $>\mathrm{C}H(\mathrm{C_6H_5})$), and 7.40 (m, 10 H, aromatic H); mass spectrum *m/e* calcd for $C_{21}H_{19}N_3O_2$ 345.148, found 345.151.

2 : 1 Adduct 6: mp 136–137° (ethyl acetate); nmr ($CDCl_3$) δ 1.90 and 2.03 (s, 3 H each, geminal CH_3's), 3.72 and 4.24 (AB doublets, $J = 16$ Hz, 1 H each, CH_AH_B), 5.95 (br s, 1 H, $-\mathrm{CH}(\mathrm{C_6H_5})$), and 7.40 (m, 15 H, aromatic H); mass spectrum *m/e* calcd for $C_{29}H_{24}N_6O_4$ 520.184, found 520.186.

2:1 Adduct 7: mp 148–149° (ethyl acetate); nmr ($CDCl_3$) δ 1.87 and 2.29 (s, 3 H each, geminal $-CH_3$'s), 4.15 and 4.65 (AB doublets, $J = 13.5$ Hz, 1 H each, CH_AH_B), 5.53 (br s, 1 H, $>\mathrm{C}H(\mathrm{C_6H_5})$), and 7.40 (m, 15 H, aromatic H); mass spectrum *m/e* calcd for $C_{29}H_{24}N_6O_4$ 520.184, found 520.187.

Iodine-Catalyzed Isomerization of 4. A solution of 38.5 mg of **4** and 1 mg of iodine in 0.30 ml of deuteriochloroform was sealed in an nmr tube and was heated in an oil bath at 110° for 10 hr. The nmr spectrum of the sample indicated that the isomerization to **5** was complete and quantitative. The solvent was removed and the product was purified by recrystallization: mp 145–146° (ether); uv max (95% ethanol) 222.5 nm (log ϵ 4.31) and 274.0 (4.30); nmr ($CDCl_3$) δ 2.13 (s, 3 H, "inside" $-\mathrm{C}H_3$ of $=\mathrm{C(CH_3)_2}$), 2.20 (s, 3 H, "outside" $-\mathrm{C}H_3$ of $=\mathrm{C(CH_3)_2}$), 4.63 (d, $J = 1.3$ Hz, 2 H, $-CH_2$), 6.77 (br s, 1 H, vinyl H), and 7.40 (m, 10 H, aromatic H); mass spectrum *m/e* calcd for $C_{21}H_{19}N_3O_2$ 345.148, found 345.143.

***cis*- and *trans*-2-Methyl-3-phenylisobutenylidenecyclopropane (9a and 9b) with PTAD. Adduct 10:** mp 151–152° (ether); uv max (95% ethanol) 222 nm (log ϵ 4.35) and 268 (3.97); nmr ($CDCl_3$) δ 1.39 (s, 3 H, "inside" $-CH_3$), 1.55 (d, $J = 6.5$ Hz, 3 H, $>\mathrm{CHC}H_3$), 2.13 (s, 3 H, "outside" $-CH_3$), 4.83 (q, $J = 6.5$ Hz, 1 H, $>\mathrm{C}H\mathrm{CH}_3$), 6.51 (br s, 1 H, vinyl H), and 7.40 (m, 5 H, aromatic H); mass spectrum *m/e* calcd for $C_{22}H_{21}N_3O_2$ 359.164, found 359.161.

Adduct 11: mp 131–132° (ether); uv max (95% ethanol) 222 nm (log ϵ 4.31) and 261 (3.27); nmr ($CDCl_3$) δ 1.80 (d, $J = 7$ Hz, 3 H, $=\mathrm{CHC}H_3$), 1.83 and 2.13 (s, 3 H each, $=\mathrm{C(CH_3)_2}$), 5.80 (q, $J = 7$ Hz, 1 H, $=\mathrm{C}H\mathrm{CH}_3$), 5.81 (br s, 1 H, $>$CH), and 7.40 (m, 10 H, aromatic H); mass spectrum *m/e* calcd for $C_{22}H_{21}N_3O_2$ 359.164, found 359.162.

2:1 Adduct 14: mp 154–155° (ethyl acetate); nmr ($CDCl_3$) δ 1.66 (d, $J = 6.4$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.95 and 2.29 (s, 3 H each, geminal $-CH_3$'s), 4.67 (q, $J = 6.4$ Hz, 1 H, $>\mathrm{C}H\mathrm{CH}_3$), 5.55 (br s, 1 H, $>\mathrm{C}H(\mathrm{C_6H_5})$), and 7.40 (m, 15 H, aromatic H).

2:1 Adduct 15: mp 134–135° (ethyl acetate); nmr ($CDCl_3$) δ 0.75 (d, $J = 6.0$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.87 and 2.33 (s, 3 H each, geminal CH_3's), 4.67 (q, $J = 6.0$ Hz, 1 H, $>\mathrm{C}H\mathrm{-CH}_3$), 5.95 (br s, 1 H, $>\mathrm{C}H(\mathrm{C_6H_5})$), and 7.40 (m, 15 H, aromatic H).

Iodine-Catalyzed Isomerization of 10. Adduct **10** was quantitatively isomerized to **12** by the procedure outlined above: mp 136.5–137.5° (ethyl acetate); uv max (95% ethanol) 222 nm (log ϵ 4.35) and 273 (4.12); nmr ($CDCl_3$) δ 1.60 (d, $J = 6.5$ Hz, 3 H, $>\mathrm{CHC}H_3$), 2.13 and 2.23 (s, 3 H each, $=\mathrm{C(C}H_3)_2$), 5.17 (q, $J = 6.5$ Hz, 1 H, $>\mathrm{C}H\mathrm{CH}_3$), 6.67 (br s, 1 H, vinyl H), and 7.40 (m, 10 H, aromatic H); mass spectrum *m/e* calcd for $C_{22}H_{21}N_3O_2$ 359.164, found 359.157.

Photoisomerization of 11. A solution of 50 mg of **11** and 0.1 mmol of benzophenone in 10 ml of benzene was purged with nitrogen and irradiated in a Pyrex vessel with a high-pressure mercury arc lamp. Samples were periodically removed and analyzed by nmr. A photostationary state equilibrium of **13** and **11** (70:30 ratio) was achieved in 3 hr irradiation time. The nmr of the photoisomer **13** ($CDCl_3$) displays peaks at δ 1.77 (d, $J = 7.0$ Hz, 3 H, $=\mathrm{CHC}H_3$), 2.10 and 2.15 (s, 3 H each, $=\mathrm{C(CH_3)_2}$), 5.94 (q, $J = 7.0$ Hz, 1 H, $=\mathrm{CHC}H_3$), 5.84 (br s, 1 H, $>\mathrm{C}H(\mathrm{C_6H_5})$), and 7.40 (m, 10 H, aromatic H).

2:1 Adduct 16 (derived as a mixture with **15** from the reaction of the 70:30 mixture of **13** and **11** with PTAD as described earlier): nmr ($CDCl_3$) δ 1.74 (d, $J = 6.4$, 3 H, $>\mathrm{CHC}H_3$), 2.02 and 2.13 (s, 3 H each, geminal CH_3's), 4.23 (q, $J = 6.4$ Hz, $>\mathrm{C}H\mathrm{CH}_3$), 5.86 (br s, 1 H, $>\mathrm{C}H(\mathrm{C_6H_5})$), and 7.43 (m, 15 H, aromatic H).

***cis*- and *trans*-2,3-Dimethylisobutenylidenecyclopropane (17a and 17b) with PTAD. Adduct 18:** mp 126–127° (ether–hexane); nmr ($CDCl_3$) δ 1.43 (d, $J = 6.5$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.73 (d, $J = 7.0$ Hz, 3 H, $=\mathrm{CHC}H_3$), 1.87 and 2.15 (s, 3 H each, $=\mathrm{C(C}H_3)_2$), 4.64 (q, $J = 6.5$ Hz, $>\mathrm{C}H\mathrm{CH}_3$), 5.59 (q, $J = 7.0$ Hz, 1 H, $=\mathrm{CHC}H_3$), and 7.32 (m, 5 H, aromatic H); mass spectrum *m/e* calcd for $C_{17}H_{19}N_3O_2$ 297.148, found 297.150.

2:1 Adduct 20: mp 160–161° (ethyl acetate); nmr ($CDCl_3$) δ 1.47 and 1.63 (d, $J = 6.4$ Hz, 3 H each, $>\mathrm{CHC}H_3$'s), 1.77 and 2.20 (s, 3 H each, geminal $-\mathrm{C}H_3$'s), 4.64 and 5.12 (q, $J = 6.4$, 1 H each, $>\mathrm{C}H\mathrm{CH}_3$), and 7.40 (m, 10 H, aromatic H); mass spectrum *m/e* calcd for $C_{25}H_{24}N_6O_4$ 472.197, found 472.202.

Photoisomerization of 18. A sample of **18** was irradiated for 30 min as described above producing a 70:30 mixture of **18** and **19**. (More prolonged irradiation led to further undefined reaction.) The nmr ($CDCl_3$) of **19** displays peaks at δ 1.44 (d, $J = 6.4$ Hz, 3 H,

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$>\mathrm{CHC}H_3$), 1.80 (d, $J = 7.0$ Hz, 3 H, $=\mathrm{CHC}H_3$), 1.99 and 2.15 (s, 3 H each, $=\mathrm{C(C}H_3)_2$), 4.91 (q, $J = 6.5$ Hz, 1 H, $>\mathrm{C}H\mathrm{CH_3}$), 5.77 (q, $J = 7.0$ Hz, 1 H, $=\mathrm{C}H\mathrm{CH_3}$), and 7.32 (m, 5 H, aromatic H).

2:1 Adduct 21 (derived as a mixture with **20**): nmr ($CDCl_3$) δ 1.50 (d, $J = 6.4$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.63 (d, $J = 6.4$ Hz, 3 H, $=\mathrm{CHC}H_3$), 1.92 and 2.11 (s, 3 H each, $=\mathrm{C(C}H_3)_2$), 4.64 (q, $J = 6.4$ Hz, 1 H, $>\mathrm{C}H\mathrm{CH_3}$), 5.07 (q, $J = 6.4$, 1 H, $=\mathrm{C}H\mathrm{CH_3}$), and 7.40 (m, 5 H, aromatic H).

2,2,3-Trimethylisobutenylidenecyclopropane (22) with PTAD. Adduct 23: mp 127–128° (ether); nmr ($CDCl_3$) 1.60 (s, 6 H), $>\mathrm{C(C}H_3)_2$), 1.70 (d, $J = 7.0$ Hz, 3 H, $=\mathrm{CHC}H_3$), 1.88 and 2.17 (s, 3 H each, $=\mathrm{C(C}H_3)_2$), 5.55 (q, $J = 7.0$ Hz, 1 H, $=\mathrm{C}H\mathrm{CH_3}$), and 7.35 (m, 5 H, aromatic H); mass spectrum *m/e* calcd for $C_{18}H_{21}N_3O_2$ 311.164, found 311.165.

Adduct 24: nmr ($CDCl_3$) δ 1.38 (d, $J = 6.7$ Hz, 3 H, $>\mathrm{CHC}H_3$)· 1.75 (s, 3 H, $-\mathrm{C}H_3$), 1.80 (s, 6 H, 2 $-CH_3$'s), 2.13 (s, 3 H, "outside" methyl of $=C(CH_3)_2$), 4.85 (q, $J = 6.7$ Hz, 1 H, $>\mathrm{C}H\mathrm{CH_3}$), and 7.35 (m, 5 H, aromatic H).

2:1 Adduct 25: 249–250° dec (ethyl acetate); nmr ($CDCl_3$) δ 1.47 (d, $J = 6.2$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.79 (s, 9 H, 3 $-CH_3$'s), 2.20 (s, 3 H, $-\mathrm{CC}H_3$), 4.69 (q, $J = 6.2$, 1 H, $>\mathrm{CHC}H_3$), and 7.40 (m, 10 H, aromatic H); mass spectrum *m/e* calcd for $C_{26}H_{26}N_6O_4$ 486.21, found 486.19.

2,2,3,3-Tetramethylisobutenylidenecyclopropane (26) with PTAD. Adduct 27: mp 184–185° (ether); uv max (95% ethanol)222 nm (log ϵ 4.31) and 255 (3.77); nmr ($CDCl_3$) δ 1.76 (s, 12 H, 4 $-\mathrm{C}H_3$'s), 1.87 (s, 3 H, $-CH_3$), and 2.13 (s, 3 H, "outside" methyl of $=C(CH_3)_2$); mass spectrum *m/e* calcd for $C_{19}H_{23}N_3O_2$ 325.179, found 325.178.

Conformational Interchange in Acyclic Hydrazines[1,2]

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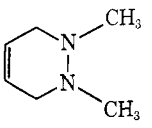
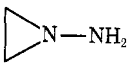
Abstract: Conformational isomerization in some acyclic hydrazines has been studied by dynamic nmr spectroscopy. The barriers to nitrogen inversion in 1,1-dibenzylhydrazine and tetrabenzylhydrazine are ($\Delta G^{\ddagger}$) 8.0 kcal/mol at −105°. Larger barriers in hydrazines with *E* substituents are attributed to hindered rotation about the NN bond. Barriers to rotation about CN bonds were observed in acetylhydrazines and picrylhydrazines.

The conformational stereochemistry of hydrazines and the barriers in them to inversion of nitrogen and rotation about the NN bond have recently attracted considerable interest.[4,5] Studies by microwave spectroscopy and electron diffraction of hydrazine[6] and some substituted hydrazines[7] have shown that the preferred configuration is one with the nitrogen lone pairs gauche to one another, and the barriers to inversion of nitrogen in tetrafluorohydrazine[8] and in cyclic hydrazines such as *N*,*N*-dimethyltetrahydropyrazine (**1**) and *N*-aminoaziridine[9] (**2**) have recently been measured. The barriers in **1** and **2** are considerably larger than those in the corresponding amines, piperidine[10] and aziridine,[11,12] a result which seems to throw doubt on the claim[6] that the barrier in hydrazine itself is much less than that in ammonia or methylamine.


1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When we began the present investigation, no barriers to nitrogen inversion seemed to have been measured by nmr spectroscopy in acyclic hydrazines. Griffith and Roberts[13] had found that the nmr spectrum of 1-benzyl-1,2,2-trimethylhydrazine remained unchanged down to −80°, implying that nitrogen inversion was still fast on the nmr time scale at this temperature.[14]

Several groups of workers[15] had shown that large NN rotational barriers exist in some di- and tetraacylhydrazines, but no barriers had been measured in other types of hydrazines.

Recent work has shown that the barriers to rotation about σ bonds connecting atoms of group V or VI elements with lone pairs of electrons can be quite large and amenable to study by the nmr method. Compounds of this type where torsional barriers have been measured include the N–S bond in sulfenamides[16] and

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