DIAZETINES, DIAZETIDINES, AND MECHANISMS OF THE ENE REACTION

by

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May, 1982

Signature of Author. . . . . Department of Chemistry, May 21, 1982

Certified by. . . . . Thesis Supervisor

Accepted by. . . . . Chairman, Departmental Committee on Graduate Students

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DIAZETINES, DIAZETIDINES, AND MECHANISMS OF THE ENE REACTION

by

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Submitted to the Department of Chemistry on May 21, 1982 in partial fulfillment of the requirement for the degree of Doctor of Philosophy.

ABSTRACT

2,3-Dihydroxylamino-2,3-dimethylbutane was oxidized with tert-butyl hypochlorite to give 3,3,4,4-tetramethyldiazetine N,N'-dioxide in moderate to high yields. 3,4-Dihydroxylamino-3,4-dimethylhexane was oxidized with tert-butyl hypochlorite at low temperature to give 3,4-diethyl-3,4-dimethyldiazetine N,N'-dioxide in low to moderate yield.

Hindered primary diamines and hindered primary amines react with dichlorodimethylsilane to give 1,3-diaza-2-silacycloalkanes and silanediamines, respectively. The 1,3-diaza-2-silacycloalkanes and silanediamines can be chlorinated on nitrogen with tert-butylhypochlorite and N-chlorosuccinimide to afford their mono- and dichloro counterparts. N,N'-Dichloro-2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane can be desilated with fluoride to give 3,3,6,6-tetramethyl-1,2-diazacyclohexene. N,N'-Dichloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane can be desilated with fluoride to give 3,3,4,4-tetramethyldiazetine. The product obtained by reacting N-chloro-N,N'-di-tert-butyl dimethyl silanediamine with fluoride was 1,2-di-tert butyldiazene.

N-Methyl and N-phenyl triazolinedione react with cis stilbene, trans stilbene, 1,1-diphenylethylene, styrene, and trans-1-phenylpropene to afford mixtures of 2:1 adducts derived from initial Diels-Alder reaction and subsequent Diels-Alder or ene reaction. 2,3-Diphenyl-p-dioxene reacts with triazolinediones to give a Diels-Alder Diels-Alder product. Diazetidines are generally not a product of reactions of triazolinediones with vinyl arenes, except in the case of indene, from which high yields of a diazetidine can be obtained. Some relative rates of reaction of vinyl arenes toward N-methyltriazolinedione were measured. The rates follow the general order styrene > 1,1-diphenylethylene > cis stilbene.

Kinetic isotope effects for the ene reaction of N-methyl and N-phenyl triazolinedione with cis, trans, and gem hexadeuterio 2,3-dimethyl-2-butene were measured. Isotope effects of 1.08, 3.8, and 5.7, respectively,

were found for reaction with N-methyltriazolinedione, and isotope effects of 1.1, 3.7, and 5.6 were found for reaction with N-phenyltriazolinedione. These isotope effects are consistent with rate-determining formation of an intermediate and subsequent C-H abstraction in a product-forming step. The structure proposed for the intermediate in this reaction is that of an aziridinium imide.

Adamantylideneadamantane and norbornylidenenorbornane react with triazolinedione to give a diazetidine, consistent with the approach of triazolindione to olefin in perpendicular planes. The X-ray crystal structure of the adduct from N-methyltriazolinedione and adamantylideneadamantane was determined. The diazetidine was found to have a distorted, nonplanar structure. The [2+2] adduct undergoes reverse reaction when heated in chloroform as does the diazetidine derived from the indene.

Triazolinedione reacts with 4,4-dimethyl-2,3-dihydropyran in benzene or acetonitrile to give a diazetidine. Reaction in methylene chloride solvent affords a vinyl urazole. Reaction in acetone-d_6 gave a diazetidine which is converted to a mixture of oxadiazine and vinyl urazole in which the oxadiazine is the major product. The formation of oxadiazine from diazetidine is evidence for an intermediate derived from the initially formed diazetidine.

Kinetic isotope effects for the ene reaction of pentafluoronitrosobenzene with cis, trans, and gem hexadeuterio 2,3-dimethyl-2-butene were measured and found to be 1.2, 3.0, and 4.5, respectively. Analogous to the ene reaction of triazolinediones with the olefins, these isotope effects are consistent with the formation of a three-center intermediate for which an aziridine N-oxide structure is proposed.

N,N'-Bis-(p-toluenesulfonyl)sulfur diimide was reacted with the hexadeuterioolefins. Isotope effects of 3.9, 3.2, and 4.9 were found for the cis, trans, and gem hexadeuterio-2,3-dimethyl-2-butene. N,N'-Bis-(p-toluenesulfonyl) sulfur diimide was reacted in a competition reaction with 2,3-dimethyl-2-butene d_0 and 2,3-dimethyl-2-butene-d_{12}. The isotope effect for this competition reaction was 1.03. These isotope effects support the rate-determining formation of a three-center intermediate, with subsequent C-H obstraction. N-Methyl and N-phenyltriazolinedione, and pentafluoronitrosobentene were also reacted with a 1:1 mixture of TME-d_0 and TME-d_{12}. Isotope effects of near unity were found for these reactions, further supporting the rate-determining formation of a three-center intermediate in these reactions.

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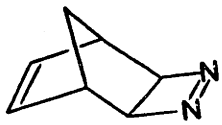
INTRODUCTION

The mechanisms of reaction and the synthesis of diazenes, diazene N-oxides, and diazene N,N'-dioxides have received much recent attention. The small ring members of these classes of compounds are of particular interest, since their reactivity has an added dimension due to substantial ring strain in the three or four membered ring cases. Diazetines, or four membered cyclic azo compounds, are a relatively unexplored class of compounds, since their study has been restricted by their limited synthetic accessibility. This thesis is concerned with approaches to the synthesis of diazetines and diazetidines (their saturated counterparts) and with the mechanisms of reaction of some compounds related to their synthesis.

Azo compounds[1] are thermally and photochemically labile, and in general decompose by a radical mechanism to give nitrogen and products derived from the radicals. Study of azo decompositions has revealed much concerning the nature of diradicals, and has given information on the question of stepwise or concerted pathways of decomposition.[2] As expected, the mode of loss of nitrogen from azo compounds is dependent on their structures[2a]. Two-bond (concerted) cleavage is usually found to occur in acyclic azoalkanes, except for unsymmetrical azoalkanes, in which one-bond (stepwise) cleavage can occur if the substituents differ greatly in their abilities to stabilize a radical.[2d,3] Two-bond cleavage has been generally established for five, six, and seven membered monocyclic azoalkanes.[4] For diazetines, two-bond cleavage would be "forbidden" by the rules of orbital symmetry.[5]

Much less is known about the reactivity of diazetines because only a few members of this class have been synthesized. 3,4-Diazatricyclo-[4.2.1.$0^{2,5}$] nona-3,7-diene 1 and 3,4-diazatricyclo [4.2.1.$0^{2,5}$] non-3-ene 2 were synthesized by cycloaddition of diethyl azodicarboxylate to quadricyclane (followed by hydrogenation in the case of 2), followed by hydrolysis and oxidation.[6] 2,3-Diazabicyclo [2.2.0] hexa-2,5-diene 3[7] and 2,3-diazabicyclo[2.2.0] hex-2-ene 4[8] were obtained by starting with the iron tricarbonyl complex of cyclobutadiene and dimethyl azodicarboxylate. The adduct of N-phenyltriazolinedione and indene was the precursor for indenodiazetine 5.[9] 3,3,4,4-Tetrafluorodiazetine 6[10] was made from the reaction of cyanogen with silver^{II} fluoride. 3,3,4,4-Tetramethyldiazetine 7[11a,11b] and 3,4-diethyl-3,4-dimethyldiazetine 8[11c,11d] were made by reduction of the corresponding N,N'-dioxides and N-oxides. Diazetine 9 was formed on irradiation of 9,9'-azoanthracene.[12] Phenyl substituted diazetines 10 and 11 have been proposed as reactive intermediates.[11d,13] The parent diazetine 12 has yet to be synthesized.

Activation energies for decomposition of diazetines have been measured for several cases: 1[6] (ΔH = 33 kcal/mole), 2[6] (ΔH = 34 kcal/mole), 5[8] ($\Delta G_{130°}$ = 21 kcal/mole), 6[10] (E_a =39 kcal/mole), and 7[11a,11b] ($\Delta G_{130°}$ = 32.5 kcal/mole). The strain energy for 3,3,4,4-tetramethyldiazetine 7 was measured and found to be 24.5 kcal/mole, based on trans-azo tert-butane as an unstrained model.[2c] Diazetines are less strained than cyclobutanes (26.2 kcal/mole), cyclobutanes (29.8 kcal/mole), and tetramethyldioxetane (30.5 kcal/mole). Engel[2c] has found that the sum of the strain energy and $\Delta H^{\ddagger}$ for thermal decomposition for medium ring cyclic azo compounds was nearly constant at about 42 to 45 kcal/mole.



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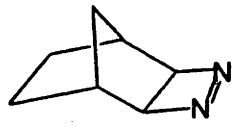

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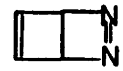

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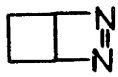

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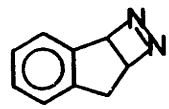

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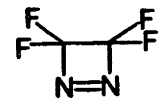

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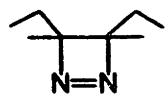

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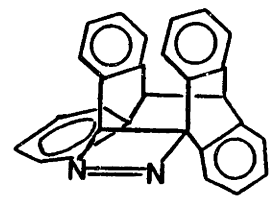

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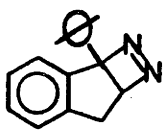

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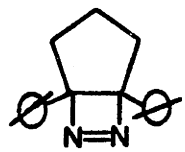

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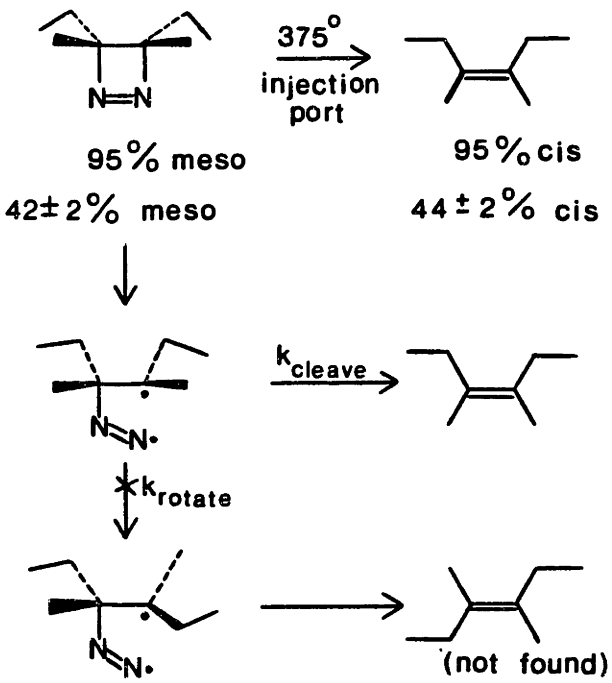
12

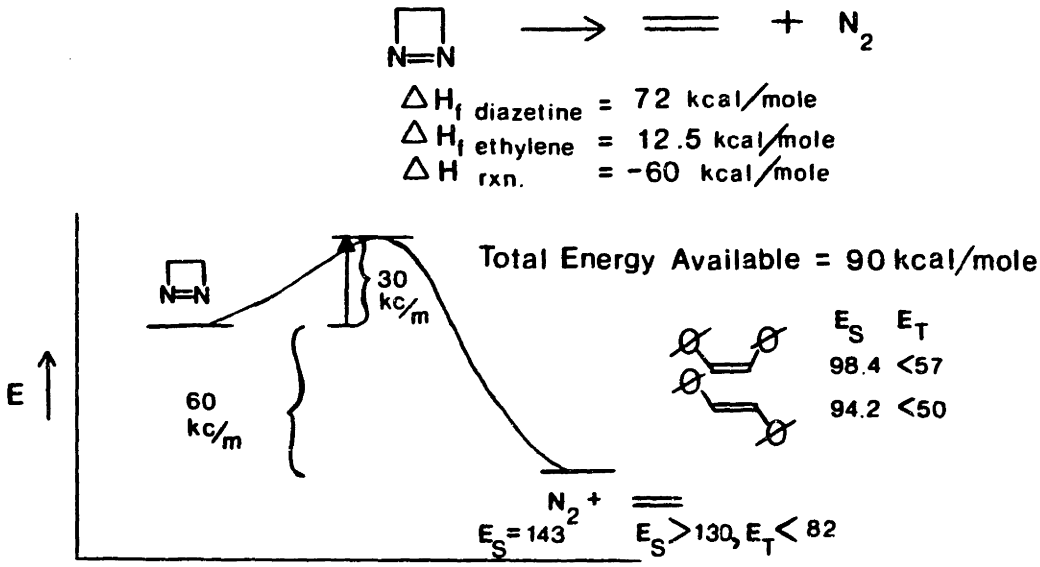
For tetramethyldiazetine, this sum is 56 kcal/mole. Thus, although tetramethyldiazetine is more strained, more energy (11 kcal/mole) is required for its thermal decomposition than for larger rings, consistent with orbital symmetry restrictions on a $[2_s + 2_s]$ decomposition path.

The question of stepwise vs. concerted loss of nitrogen from diazetines was addressed by White.[11c,11d] 3,4-Diethyl-3,4-dimethyldiazetine was synthesized, and the stereochemistry of its thermal decomposition was investigated.

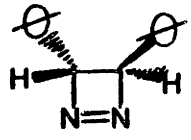


The decomposition was found to proceed with retention of stereochemistry, consistent with a mechanism in which the C-N bond is broken to form a biradical. The diazenyl radical then fragments with loss of nitrogen before bond rotation occurs to give net retention of stereochemistry in the resulting olefin products. The symmetry-allowed possibility of synchronous loss of nitrogen by a 2a (olefin) + 2s (nitrogen) pathway is therefore excluded.

Estimation of the total energy available on thermal decomposition of diazetines has indicated the possibility of electronically excited state products from decomposition of an appropriately substituted diazetine. The heat of formation of unsubstituted diazetine 12 was calculated by group additivity by White[11c,11d] to be 72 kcal/mole. Given that the heat of formation of ethylene is 12.5 kcal/mole, the expected heat of reaction for decomposition of diazetine 12 to nitrogen and ethylene is about 60 kcal/mole.[11d] Diazetine 12 is expected to have an activation energy requirement for decomposition of about 30 kcal/mole. which gives a total of about 90 kcal/mole energy available to products. Choice of the appropriately substituted diazetine thus might allow for the generation of a thermally produced excited singlet or triplet olefin. Retention of stereochemistry in the decomposition of meso and dl 3,4-diethyl-3,4-dimethyldiazetine to cis and trans 3,4-dimethyl-3-hexene (E_T<75 kcal/mole) indicates that the excited triplet state has not been formed;[11c] the excited singlet state is too energetic (130 kcal/mole) to be reached via this decomposition.



There is considerable interest in the diazetines related to stilbene, 13 and 14, for which an even bigger energy difference may exist between energy from decomposition and energies of the first excited triplet states. For cis stilbene, E_S = 98.4 kcal/mole and E_T<57 kcal/mole;



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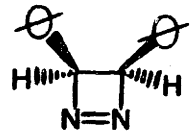


14

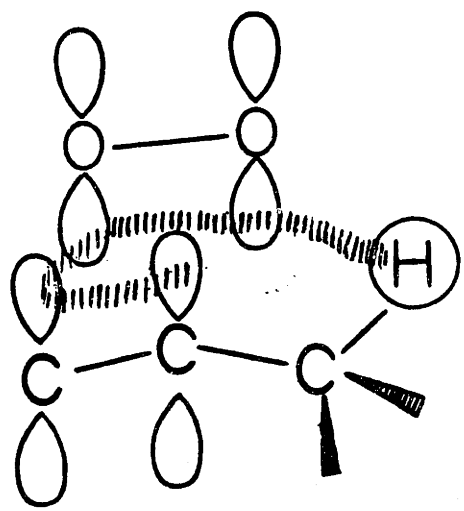
for trans stilbene, E_S = 94.2 kcal/mole and E_T<50 kcal/mole.[15] Thus, dl diazetine 13 would decompose to yield trans stilbene; crossover to T_1 would result in the formation of some cis stilbene. Little is known concerning processes which involve thermal generation of electronically excited states, and diazetines such as 13 and 14 would provide means by which to probe this area.

The synthesis of 13 and 14 and related aryl substituted diazetines provides unusual challenges, in that the activation energies for the decomposition of aryl substituted diazetines may be significantly lower than their alkyl substituted counterparts. (The maximum activation energy for diazetine 11 is estimated to be 22 Kcal/mole.[11d,13b]) The free energy of activation (130°) for decomposition of indenodiazetine 5 was measured and found to be 21 kcal/mole,[9] about 10 kcal/mole less than for alkyl substituted diazetines. In addition to their reduced kinetic stability, the synthesis of 13 and 14 must accommodate the benzylic hydrogens found in their structures.

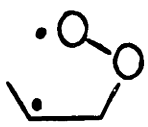
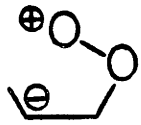
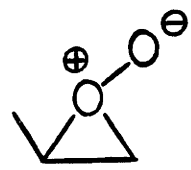
In connection with efforts to synthesize diazetines, we have had occasion to examine the mechanisms of reaction of some potential precursors to diazetidines, N-phenyl and N-methyltriazolinedione. Like singlet oxygen, these electrophiles are of utility in the functionalization of olefins. The reactivities of singlet oxygen[16] and triazolinedione are parallel in many respects: both compounds have the ability to react as dienophiles in Diels Alder reactions, as enophiles in the ene reaction of olefins, and as electrophiles in [2+2] cycloadditions.

Singlet oxygen has been found to be reactive toward phenyl substituted ethylenes through a variety of pathways to give products derived from Diels Alder reactions involving the double bond and the aromatic ring, and products derived from [2+2] cycloaddition to the central double bond.[16] The control of regiochemistry in triazoline-dione-olefin reactions in which diazetidine products are possible is somewhat unexplored; study of this regiochemistry is of importance to the understanding of the mechanism of reaction for triazolinedione.

In the same sense that the mode of loss of nitrogen from diazetines (stepwise vs. synchronous) is of mechanistic interest, the mode of addition of azo electrophiles to olefins has drawn attention,[17] and is expected to be dependent upon the structure of the azo compound. The analogous addition of singlet oxygen to double bonds has been studied in detail; several mechanisms for its ene reaction with alkenes have been proposed. A concerted mechanism has been supported by the absence of solvent effects for the $^1O_2$-olefin reaction and by the requirement for properly aligned C-H bonds in conformationally rigid cyclohexanes.[18]



The concerted pathway, however, has been superceded by an abundance of evidence which favors a stepwise mechanism requiring the formation of a discrete intermediate. Among possible structures for an intermediate are a biradical, or zwitterion, or a perepoxide. The energetics for

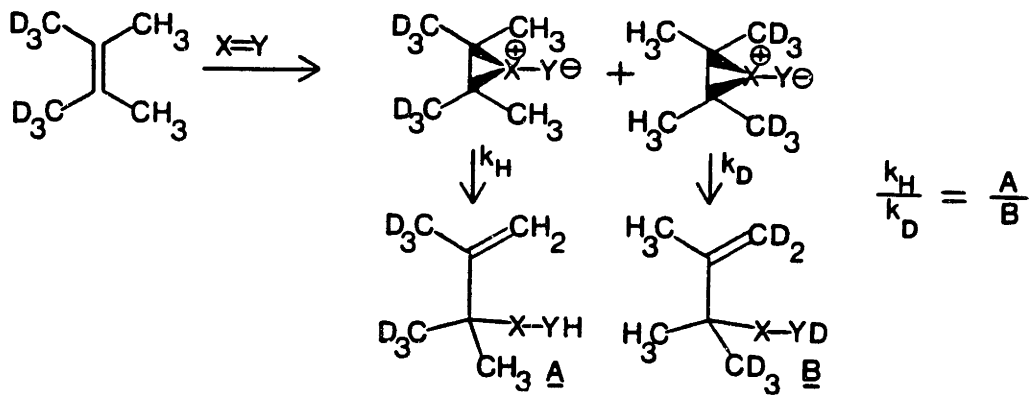




these potential intermediates have been evaluated by several investigators using varied methods of calculation.[18] Using frontier orbital methods, Kearns[19] reported that the preferred mode of addition leads to the formation of a perepoxide. Fukui's[20] semiempirical calculations (CNDO-2-CI) indicate that the perepoxide is not a true intermediate although addition to give a perepoxide is energetically favorable. Studies by Dewar and Thiel,[21] using semiempirical MINDO/3 methods on the reaction of singlet oxygen with ethylene and with several substituted olefins support a discrete perepoxide intermediate for most olefins, except for electron-rich olefins which react <u>via</u> a zwitterionic intermediate. Their calculations predict a perepoxide derived from propene to be more stable than the reagents. Ab initio calculations (GVB-CI) by Harding and Goddard[22] place a biradical at the energy minimum, 9 kcal/mole above singlet oxygen and ethylene reagents, and place the perepoxide 8 kcal/mole above the biradical. Analysis of the reaction in terms of ab initio energies and thermochemical estimates by Harding and Goddard[18] support a biradical intermediate for the gas phase reaction,

while in solution both a biradical or a biradical having zwitterionic character are possible.

Stephenson has devised several tests using kinetic hydrogen isotope effects as probes for the detection of an intermediate in this reaction. Among them is a test which is diagnostic for the formation of an intermediate having the geometry of a perepoxide.[23] Cis, trans, and gem hexadeuterio-2,3-dimethyl-2-butene were allowed to react separately with singlet oxygen. The kinetic isotope effect, k_H/k_D, is found by measuring the ratio of H containing product to D containing product, and the kind and size of the isotope effect is related to the type of intermediate formed. For the case of the cis deuterated olefin, two isomeric intermediates with the geometry of a perepoxide can be formed, one of which leads only to the abstraction of hydrogen, and one of which leads only to the abstraction of deuterium. In the absence of steric and electronic effects, the two perepoxides are formed from singlet oxygen in equal amounts. For the cases of the trans or gem deuterated olefin, only one perepoxide intermediate is formed; it has the choice of hydrogen or deuterium abstraction. An intermediate with a perepoxide-like geometry would result in a small kinetic isotope effect for reaction with the trans or gem olefin since this mechanism allows for competition on one side of the olefin, but not across the central bond. An open biradical or zwitterionic intermediate would allow competition across the central bond; the cis and trans deuterated compounds would have the same kinetic isotope effect.

The isotope effects from reaction of singlet oxygen with the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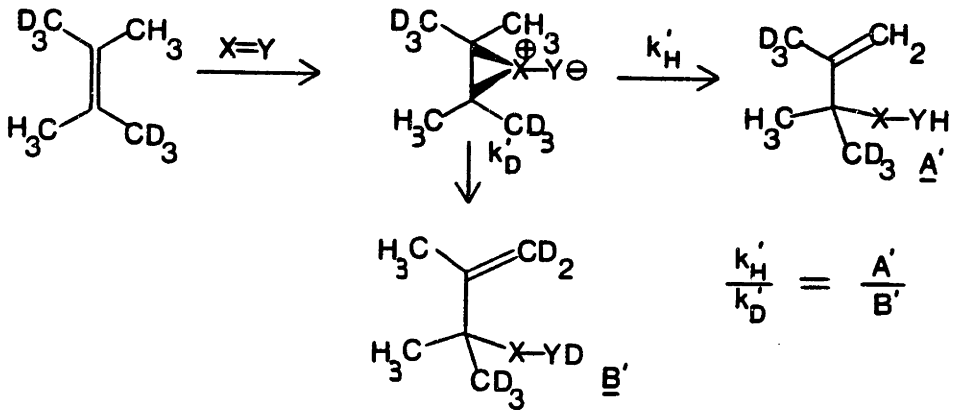
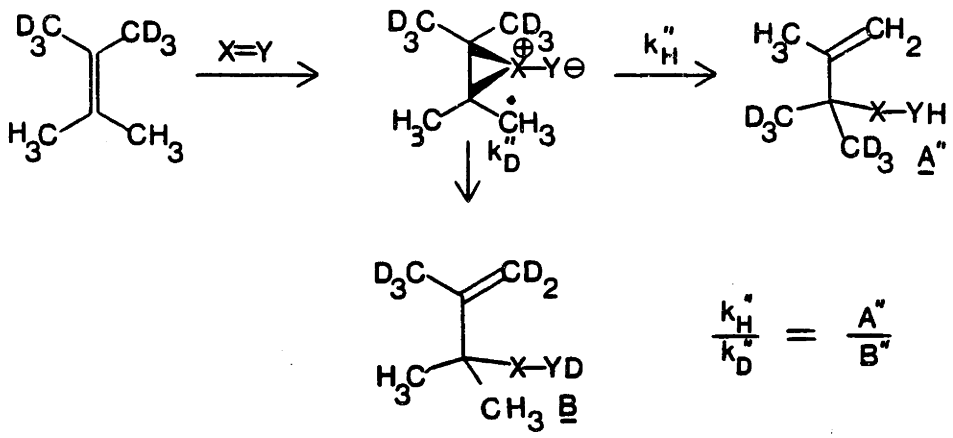
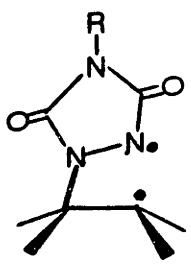
k_H
k_D
A
B
$\frac{k_H}{k_D} = \frac{A}{B}$

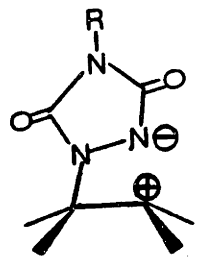

X=Y
k'_H
k'_D
A'
B'
$\frac{k'_H}{k'_D} = \frac{A'}{B'}$

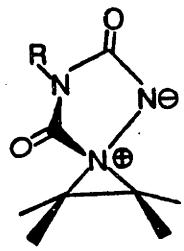

X=Y
k''_H
k''_D
A''
B
$\frac{k''_H}{k''_D} = \frac{A''}{B''}$

various hexadeuterated olefins support the perepoxide intermediate. Stephenson and coworkers[23] found that the cis hexadeuterio-2,3-dimethyl-3-butene gave an isotope effect of 1.0 to 1.08, while the trans olefin gave an isotope effect of 1.38 to 1.41. The isomeric gem-d_6 olefin was reported to give an isotope effect of 1.45.[24] These results are consistent with a mechanism in which there is initial C-O bond formation accommodating a perepoxide intermediate, and subsequent hydrogen abstraction.

Similar mechanistic possibilities exist for the ene reaction of triazolinedione with olefins. Possible intermediates in a stepwise process include open biradical or dipolar forms, and a perepoxide-like aziridinium imide. A 1,4-dipolar intermediate in the reaction of tri-







azolinedione with indene was suggested by von Gustorf[25] through trapping experiments and studies of solvent effects. The formation of oxadiazines from reaction of triazolinediones with vinyl ethers and ketones, reported by Butler,[26] has also been interpreted in terms of a 1,4-dipolar intermediates. For the reaction of simple disubstituted olefins with triazolinediones, Butler[27] has found that solvent effects on rate are generally small. Triazolinedione (TAD) is 10^4 times as

reactive toward olefins as dimethyl azodicarboxylate; a novel intermediate such as an aziridinium imide might form with more ease in the reaction of TAD with olefins than from dimethyl azodicarboxylate and olefins. Rearrangement of an aziridinium imide to ene product has precedent in the thermal reaction of aziridine N-oxides to hydroxylamines, reported by Baldwin[28] in 1971. The mechanism of ene addition of triazoline dione to olefins has been little studied; herein are reported some results of efforts towards its elucidation.

Other questions related to the mechanism of the triazoline dione-olefin reaction involve the role of the lone pair electrons on nitrogen. This question can be addressed by a probe of the mechanism of ene reaction of olefins with other compounds having similar heteroatomic structure to TAD; i.e., containing N-O and N-S bonds. Nitroso compounds undergo the ene reaction with olefins; in analogy to the singlet oxygen-olefin reaction, this addition might proceed via an aziridine N-oxide intermediate. Aziridine N-oxides have been observed spectroscopically by Baldwin and coworkers as products of low temperature reaction of aziridines with ozone.[28] On warming, the N-oxides rearrange to form the same allylic hydroxylamine products derivable from the olefin-RNO reaction.

The geometry and polar characteristics of an aziridine N-oxide intermediate are expected to differ from that of a perepoxide or aziridinium imide in that this species possesses greater steric bulk and is not symmetrical. Study of the effect of nitroso structure on this reaction is limited by the instability of the hydroxylamine product toward oxygen. These studies have thus been restricted to the ene

reaction of pentafluoronitrosobenzene, which undergoes ene reactions with olefins to give high yields of a hydroxylamine of fair to moderate stability.[29]

Mechanisms of reactivity of enophiles containing N-S bonds have received some attention. Bis(N-p-toluenesulfonyl) sulfodiimide (TsNSNTs) and olefin first form the ene product containing a bond from sulfur to alkene. The ene product then undergoes [2,3] sigmatropic rearrangement.[30] A study of an N-S bonded enophile has been included in these investigations.

These studies explore differences in reactivity of electrophiles that undergo ene reaction with olefins which have the possibility of proceeding via three-centered, perepoxide-like intermediates. Evidence of the relative stabilities of such intermediates is of interest in that it provides information on bonding character in the intermediates and bonding capability for the enophile. Insight into these reaction mechanisms is of potential value in the synthesis of related compounds, such as diazetines, for which access is presently limited.

The Results and Discussion section is comprised of two parts:

I. Approaches to the Synthesis of Diazetines and Related N,N'-Dioxides;

II. Mechanism of the Addition of Triazolinedione and Related Compounds to Olefins in the Ene Reaction.

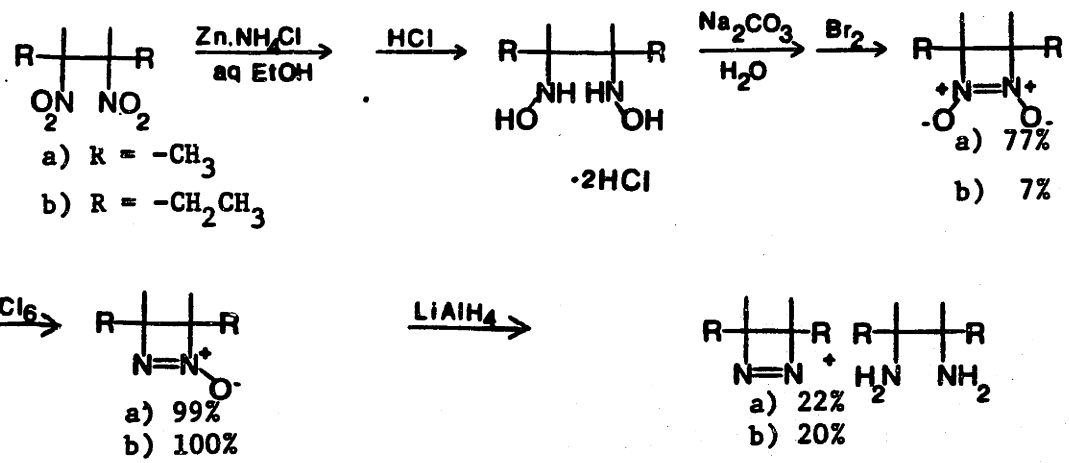
RESULTS AND DISCUSSION

I. Approaches to the Synthesis of Diazetines and Diazetine N,N'-Dioxides.

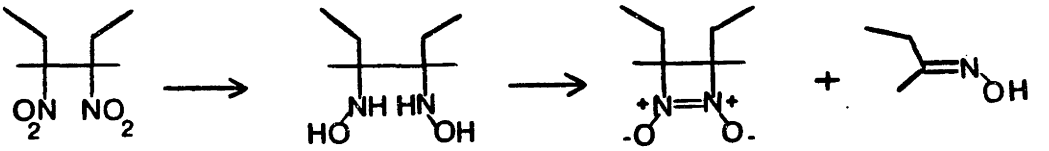
Because of their ring strain and thermal instability, diazetines as a class of compounds are synthetically challenging targets. Most amine oxidations, successful for the preparation of acyclic and larger ring cyclic azo compounds, lead to cleavage of 1,2-diamines. Diazetines have been synthesized primarily through the reduction of the corresponding diazetine N,N'-dioxides, and through the hydrolysis of amides or urazoles obtained by [2+2] cycloaddition of electrophiles to olefins. A few diazetidines have been made by displacement of bromide from 1,2-dibromides by alkyl hydrazines.[31] This work is focused on the synthesis of alkyl and aryl substituted diazetines.

Oxidation of Aliphatic 1,2-Dihydroxylamines

Recent efforts toward the synthesis of tetraalkyldiazetines in this group have involved the oxidation of 1,2-dihydroxylamines to diazetine N,N'-dioxides (azo dioxides), which are subsequently reduced to azo compounds in two steps.[11] Tetraalkyldihydroxylamines are available in moderate-to-low yields from the corresponding dinitro compounds.[32]



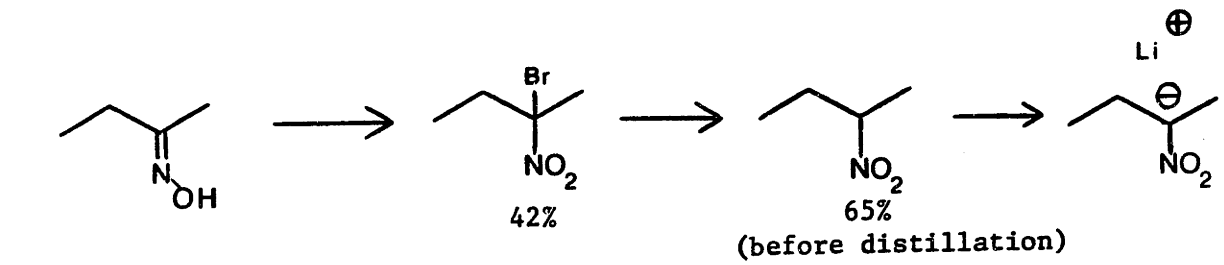
Zinc reduction of 3,4-dimethyl-3,4-dinitrohexane followed by bromine oxidation has been reported to give only 7% (isolated yield after recrystallization) of 3,4-diethyl-3,4-dimethyl diazetine N,N'-dioxide.[11c,11d] The low yields in this step can be explained by a Grob fragmentation of the intermediate dihydroxylamine or a derivative thereof, related to greater crowding in this system.



Improved methods of effecting the conversion of dinitro compound to azo dioxide were sought; a study of the effect of the reaction conditions and procedures for the preparation of dihydroxylamine was undertaken. Initially, the synthesis of 3,3,4,4-tetramethyldiazetine N,N'-dioxide was explored. Oxidation of aqueous solutions of 2,3-dihydroxylamino-2,3-dimethylbutane (obtained by sodium bicarbonate neutralization of crude hydroxylamine salts) with two to three equivalents of bromine gave the azo dioxide in ca. 70% isolated yield (Table VI). Dimethyl azodicarboxylate and chloranil (methylene chloride solvent) gave substantial amounts of acetone oxime as a side product. Oxidation of a suspension of the dihydroxylamine hydrochloride salt in methylene chloride with tert-butyl hypochlorite (in the presence of sodium bicarbonate) produced encouraging results; 63% of the azo dioxide was obtained.

Oxidation of 2,3-dihydroxylamino-2,3-dimethylbutane as the free base was also investigated (Table VII). In accord with reports by Greene and Gilbert,[11a] high yields (ca. 95%) of azo dioxide can be obtained by oxidation in water with 10 equivalents bromine. High yields of azo dioxide can also be obtained through the use of only 2.4 equivalents bromine. In addition, the dihydroxylamine can also be oxidized in methylene chloride with tert-butyl hypochlorite; under these conditions, an excess of tert-butyl hypochlorite is desirable.

The previously described findings were applied toward the synthesis of 3,4-diethyl-3,4-dimethyl diazetine N,N'-dioxide from 3,4-dimethyl-3,4-dinitrohexane. 2-Bromo-2-nitrobutane (obtained by reaction of N-bromosuccinimide with 2-butanone oxime) was reduced with sodium borohydride to afford 2-nitrobutane; the dinitro alkane was prepared by coupling of 2-bromo-2-nitrobutane with the lithium salt of 2-nitrobutane.



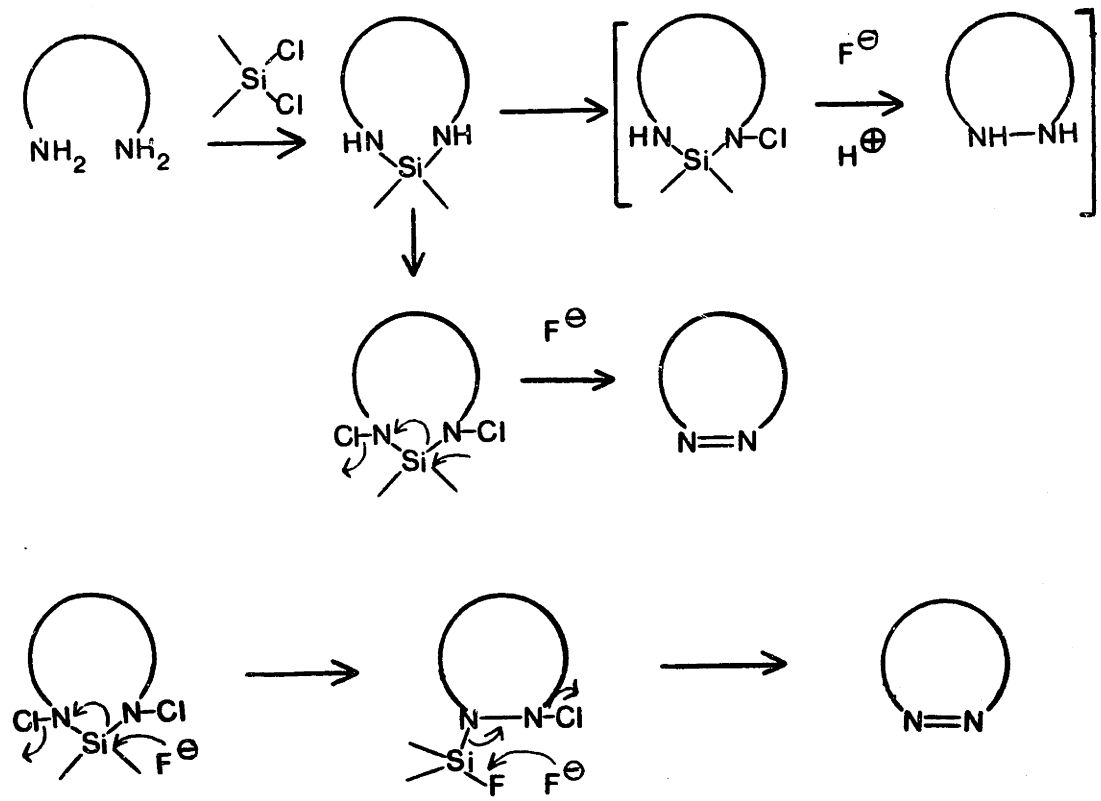
The 3,4-dimethyl-3,4-dinitrohexane obtained by this method was found to consist of a 1:1 mixture of diastereomers; all subsequent experiments involving this compound were performed using this 1:1 mixture. This reaction sequence was found to be preferable to that of Barnes and Patterson;[33] the use of ozone, iodine, and chlorine have been avoided.

Some improvement in the yield of 3,4-diethyl-3,4-dimethyl diazetine N,N'-dioxide was made through the use of tert-butyl hypochlorite and lowered reaction temperatures in methylene chloride solvent (Table VIII). In accord with the findings of White,[11d] the method found to be useful in the preparation of 3,3,4,4-tetramethyldiazetine (oxidation with Br_2 in water) gave 2-butanone oxime as a side product and low isolated yields of azo dioxide. Modest yields (ca. 30%) of azo dioxide could be obtained through the use of tert-butyl hypochlorite; with the use of low reaction temperatures, high yield recovery (ca. 70%) of products is possible, but the separation of a 2.3 to 1 mixture of azo dioxide to oxime remains. The use of tert-butyl hypochlorite for this oxidation, however, is a significant improvement, and low reaction temperatures minimizes C-C cleavage of dihydroxylamines. In view of the restrictions of the previously described methods, attention was focused on the development of a new milder synthesis of azo compounds that would be applicable to the problem of diazetine synthesis.

Desilation of N-Chloro and N,N-Dichlorodimethylsilanediamines

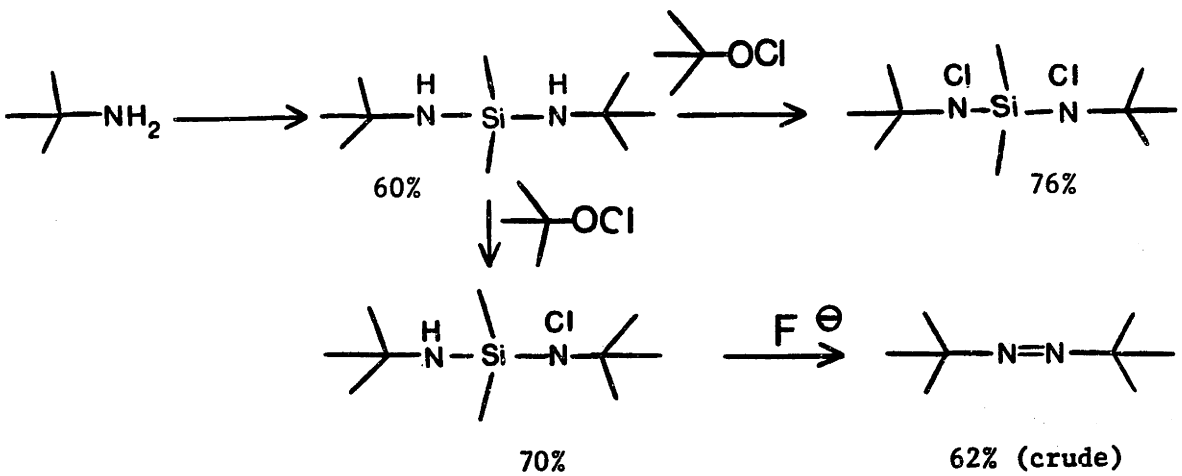
In view of the need for mild methods of coupling amines to azo compounds, efforts were made to develop a method that might be applicable to diazetine synthesis. Cyclic azo compounds can be made by the reaction of a diamine with hydrogen peroxide in the presence of sodium tungstate,[11a] but reaction of 2,3-diamino-2,3-dimethylbutane with sodium tungstate and hydrogen peroxide failed to give any diazetine product.[11d] The new synthetic approach for converting diamines to azo compounds and applicable to diazetine synthesis is shown in Figure 1.

Figure 1. Synthesis of Azo Compounds from Silanediamines.



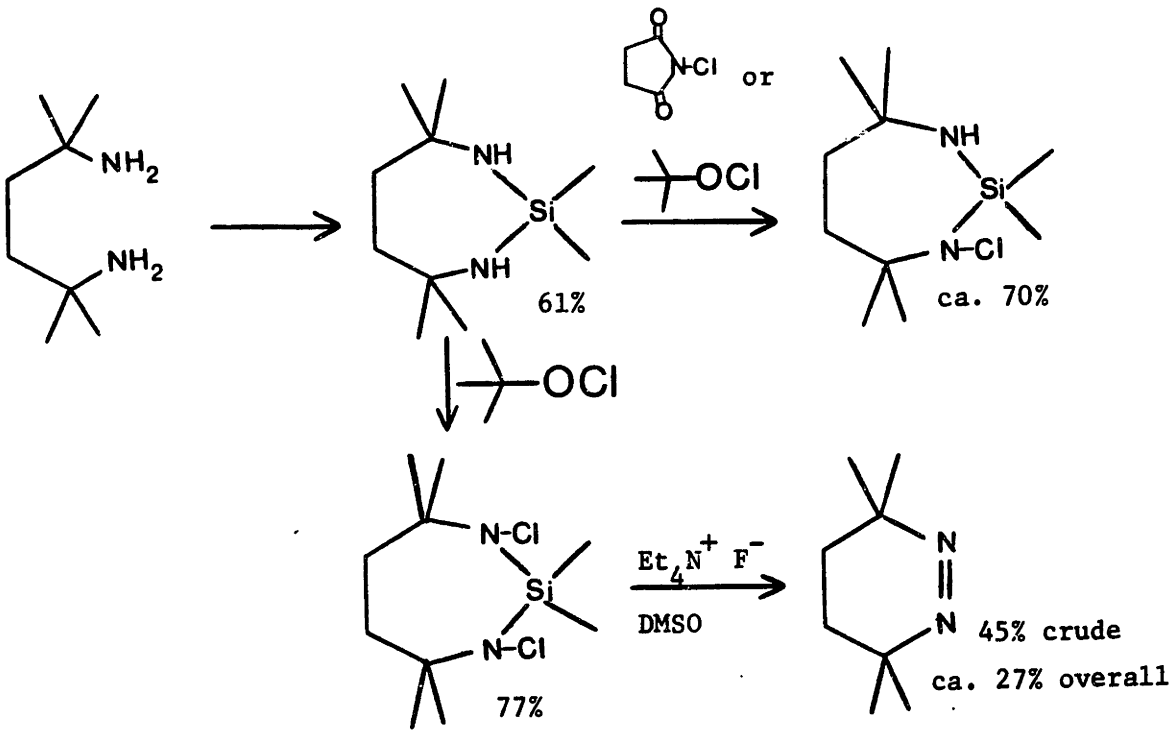
primary and secondary amines with chlorosilanes is known to afford aminosilanes,[34] but only a few examples of these are derived from diamines. Compounds containing an N-Si bond are sensitive toward heat and moisture; hydrolysis occurs readily on exposure to the atmosphere. Aminosilanes derived from primary amines can be chlorinated on nitrogen;[35] the products are somewhat sensitive to heat but are much more stable toward hydrolysis than their precursors.

The conversion of tert-butyl amine to 1,2-di-tert-butyldiazene has been accomplished through this sequence. Reaction of tert-butylamine with dichlorodimethylsilane in hexane gave N,N'-di-tert-butyldimethylsilanediamine in 60% yield. Chlorination with tert-butyl hypochlorite in methylene chloride gave N-chloro-N,N'-di-tert-butyl dimethyl silanediamine and N,N'-dichloro-N,N'-di-tert-butyl dimethyl silanediamine. Bromination of the starting silanediamine could be effected with N-bromosuccinimide, but the products were found to be quite unstable toward air and heat, and decomposed rapidly and exothermically on exposure to air.



Reaction of N-chloro-N,N'-di-tert-butyl dimethyl silanediamine with tetraethyl ammonium fluoride in dimethyl sulphoxide gave 62% of a yellow oil that was found to contain 1,2-di-tert-butyl diazene as the major product by NMR and GLC.

This methodology was next applied toward the synthesis of a cyclic diazene, 3,3,6,6-tetramethyl-1,2-diazacyclohexene. 2,2,4,4,7,7-

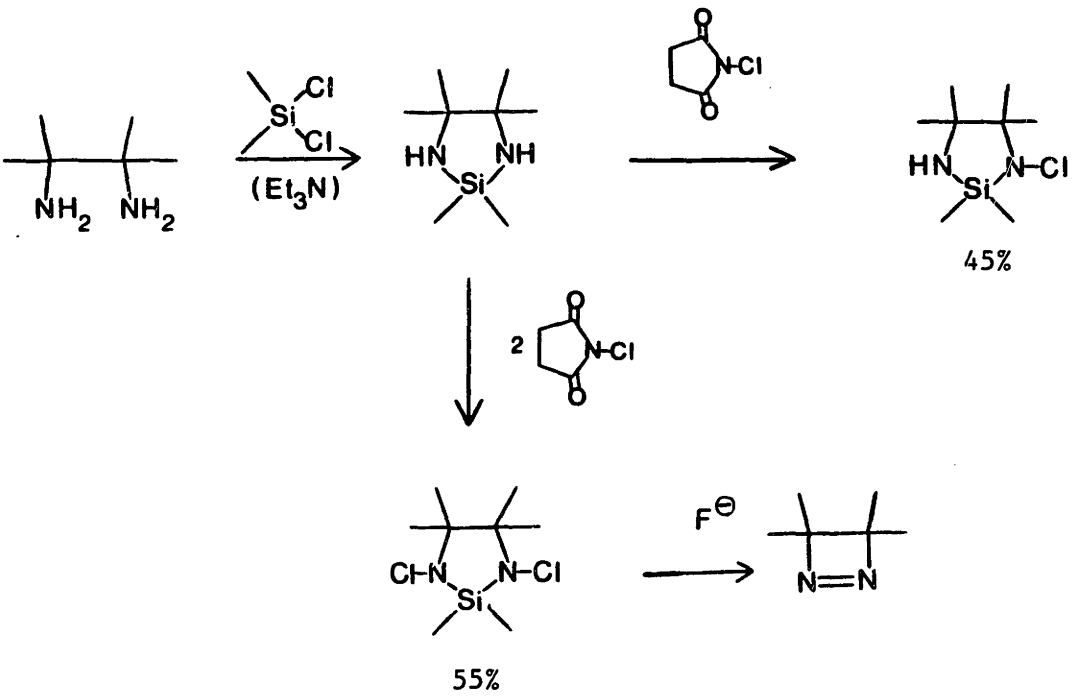


Hexamethyl-1,3-diaza-2-silacycloheptane was synthesized by the reaction of dichlorodimethyl silane with 2,5-diamino-2,5-dimethyl hexane. This compound is the first example of a cyclic silanediamine in which the nitrogen bears a hydrogen atom; other known cyclic silanediamines are alkylated or silylated on nitrogen. 2,2,4,4,7.7-Hexamethyl-1,3-diaza-2-silacycloheptane was also prepared by reaction of the diamine with dichlorodimethyl silane in the presence of triethylamine in reduced

yields. Reaction of 1,3-diaza-2-silacycloheptane with tert-butyl hypochlorite or N-chlorosuccinimide gave N-chloro-2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane and N,N'-dichloro-2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane in good yields. Treatment of N,N'-dichloro-2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane with tetraethyl ammonium fluoride in diemthyl sulphoxide gave a yellow oil in 45% yield; the oil was found to contain 60% 3,3,6,6-tetramethyl-1,2-diazacyclohexene by GLC for an overall yield of ca. 25%. This method compares unfavorably with the synthesis of this azo compound from the diamine, sodium tungstate, and hydrogen peroxide.

Extension of these methods to the synthesis of 3,3,4,4-tetramethyl diazetine was successful. 2,3-Diamino-2,3-dimethylbutane was silated with dichlorodimethylsilane in pentane in the presence of triethylamine to afford 2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane in 44% yield. This compound was extremely sensitive to heat and moisture. Chlorination with N-chlorosuccinimide gave N-chloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane and N,N'-dichloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane as waxy yellow solids in moderate yields. Reaction of the latter with fluoride ion under a variety of conditions gave 3,3,4,4-tetramethyldiazetine in yields of 16 to 42% (Table IX).

The synthesis of azo compounds form N-chloro and N,N'-dichloro-1,3-diaza-2-silacycloalkanes is likely to have limitations. This method may be restricted by the availability of appropriate diazasilacycloalkanes and acyclic silanediamines. The accessibility of these compounds is expected to be limited to cases in which carbon adjacent to the



amino nitrogen is sufficiently substituted such that the amine reacts with only one mole of silyl chloride. The examples studied are structures in which the amine is hindered by the effects of an adjacent quaternary carbon. 2,2,4,4,7,7-Hexamethyl-1,3-diaza-2-silacycloheptane and 2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane are the first known members of these classes of 1,3-diaza-2-silacycloalkanes in which both nitrogens are substituted with hydrogen atoms. The synthesis of other members of these ring systems in which the amine is less hindered may be less successful; the more reactive amine may react with more than one mole of silyl chloride, and the resulting N-Si bond may be more susceptible to hydrolysis. Reaction of ethylene diamine with dichlorodimethyl silane gave a mixture of products (nonvolatile, probably polymeric), consistent with previous failure to isolate 2,2-dimethyl-1,3-diaza-2-silacyclopentane.[36] Similarly, reaction of dichlorodimethyl silane

with 1,2-diamino-1,2-diphenylethane gave no volatile products.

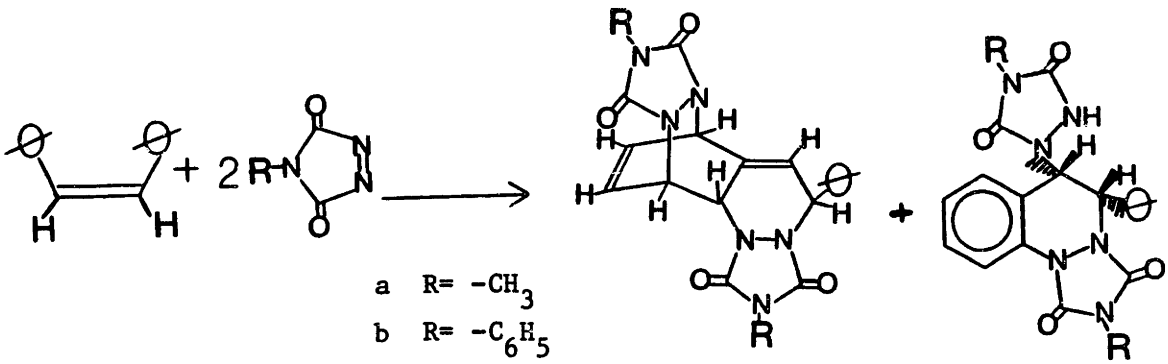
The successful conversion of 2,3-diamino-2,3-dimethylbutane to 3,3,4,4-tetramethyldiazetine by the previously described route led to explorations of the synthesis of the diamine, presently avaiable from the corresponding dinitro compound by reduction with tin and HCl.[37] 2,3-Dimethyl-2,3-dinitrobutane was reduced under a variety of conditions (Table V).

Hydrogenation of the dinitrobutane under acidic conditions using palladium on carbon as a catalyst gave moderate yields of diamine or salts of the diamine. This method may be preferable to tin reduction for the preparation of 2,3-diamino-2,3-dimethylbutane primarily for reasons of convenience.

Cycloadditions of Triazolinediones to Phenylethylenes

The [2+2] cycloaddition reaction of triazolinedione with a phenyl-substituted ethylene to give a diazetidine, followed by hydrolysis and oxidation, is an attractive potential route to phenyl-substituted diazetines. Von Gustorf and coworkers[25] found that reaction of N-phenyltriazolinedione with indene afforded a diazetidine to the diazetidine; Pincock[9] has reported the conversion of this diazetidine to the diazetine. In efforts toward the synthesis of diazetines 13 and 14, related to stilbene, reactions of triazolinediones with stilbenes and related olefins have been explored.

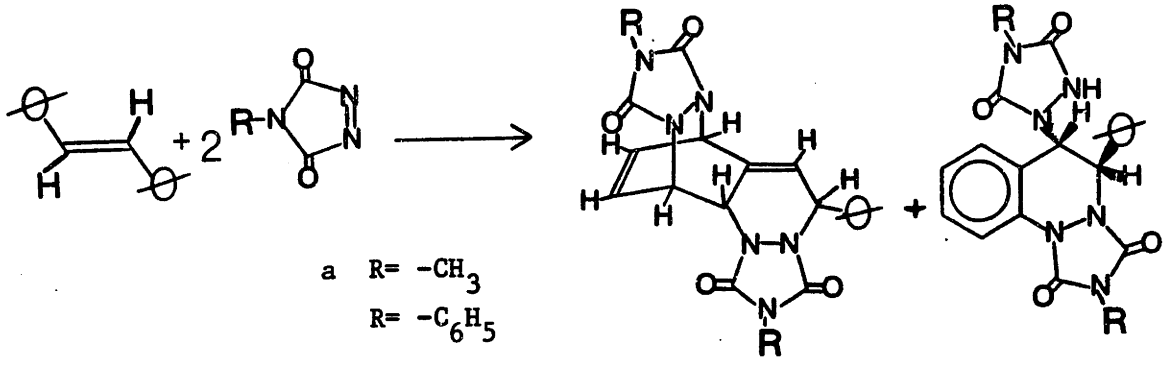
cis Stilbene was allowed to react with N-methyl and N-phenyltriazolinedione in methylene chloride solvent. The only product was the 2:1 (TAD: stilbene) adduct 15 formed by two successive Diels-Alder reactions of triazolinedione to stilbene. The stereochemistry of this adduct has been assigned as shown. The first Diels-Alder reaction proceeds with retention of stereochemistry; addition of the second molecule of TAD occurs from the less hindered side. A 1:1 adduct could not be isolated from the reaction mixture, even when low temperature or dilution conditions were used. Reaction of cis stilbene with triazolinedione in benzene or diethyl ether gave a second 2:1 adduct 16 as a minor product, formed by initial Diels-Alder reaction of TAD to cis stilbene, followed by ene reaction of a second equivalent of TAD. The yields of products were estimated by high field NMR. The stereochemistry of the Diels-Alder-ene adduct 16 was not determined because of the low yield of this product.



a R= $-CH_3$
b R= $-C_6H_5$

Solvent	15	16
Et_2O	68%	32%
Benzene	78%	22%
CH_2Cl_2	100%	0%

trans Stilbene has been reported to react with TAD to afford a 2:1 adduct formed by initial Diels-Alder reaction followed by ene reaction.[38] This reaction was reinvestigated in efforts to ascertain whether any diazetidine was formed. We have identified and isolated a second



a R= $-CH_3$
R= $-C_6H_5$

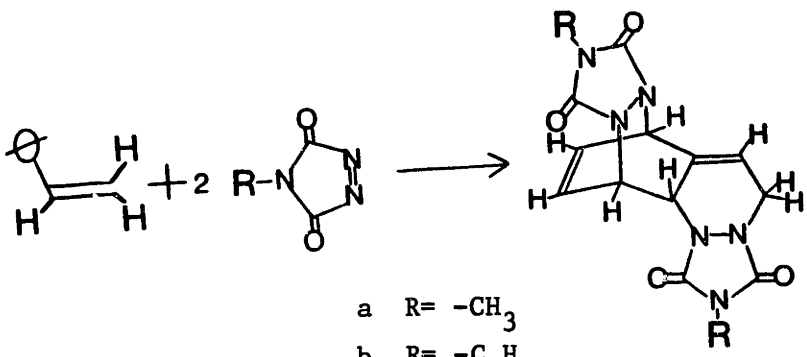
Solvent	17	18
Et_2O	13%	87%
CH_2Cl_2	30%	70%
Benzene	30%	70%
DMSO	65%	35%

product from this reaction, the 2:1 adduct 17 , formed by two successive Diels-Alder reactions. The relative yields of the two products is dependent on the solvent; in diethyl ether, methylene chloride, and benzene, the major product is the Diels-Alder-ene adduct 18 , while in dimethyl sulfoxide, 17 is formed as the major product.

Diels-Alder-Diels-Alder adduct 17 has been assigned the stereochemistry shown, and forms in a manner analogous to that described for the corresponding product from the cis olefin. The Diels-Alder-ene adduct 18 from trans stilbene was previously assigned the trans stereochemistry shown. Examination of the NMR spectrum (270 MHz) of the crude product mixture from reaction of TAD with cis stilbene revealed essentially no difference between the Diels-Alder-ene adduct 16 derived from cis stilbene and the Diels-Alder-ene adduct 18 derived from trans stilbene. However, since the Diels-Alder-ene product from cis-stilbene was not isolated, we do not know whether these two ene products are the same or not. Since the Diels-Alder-Diels Alder adducts from cis and trans stilbene do differ, we expect that the Diels-Alder-ene adducts also differ (in the stereochemistry at the carbon holding the C_6H_5 group). Analysis of the NMR spectral data (Table I) has not afforded a basis for this assignment. There is no evidence for loss of stereochemistry in the formation of any of the previously described 2:1 adducts and therefore no evidence for a mechanism involving formation of an intermediate.

A 2:1 adduct formed by two successive Diels-Alder reactions was reported as the product of reaction of N-phenyltriazolinedione and styrene in acetone by Cookson.[39] The reaction was reinvestigated, and

two products were found. Product yields are shown below.



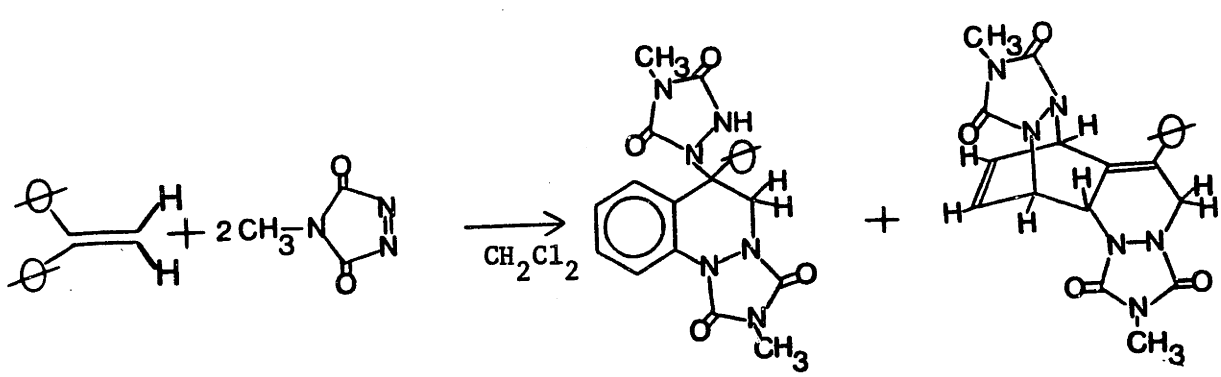
a R= $-CH_3$
b R= $-C_6H_5$

19 20

	Solvent		
a	DMSO	25%	75%
b	CH_2Cl_2	30%	70%
b	acetone	25%	75%

No diazetidine product was apparent in the crude reaction mixture.

N-Methyltriazolinedione was allowed to react with 1,1-diphenylethylene for comparison purposes. Reaction in methylene chloride gave close to a 2:3 ratio of Diels-Alder-Diels-Alder adduct 21 to Diels-Alder-ene adduct 22. Again, a diazetidine product was not apparent



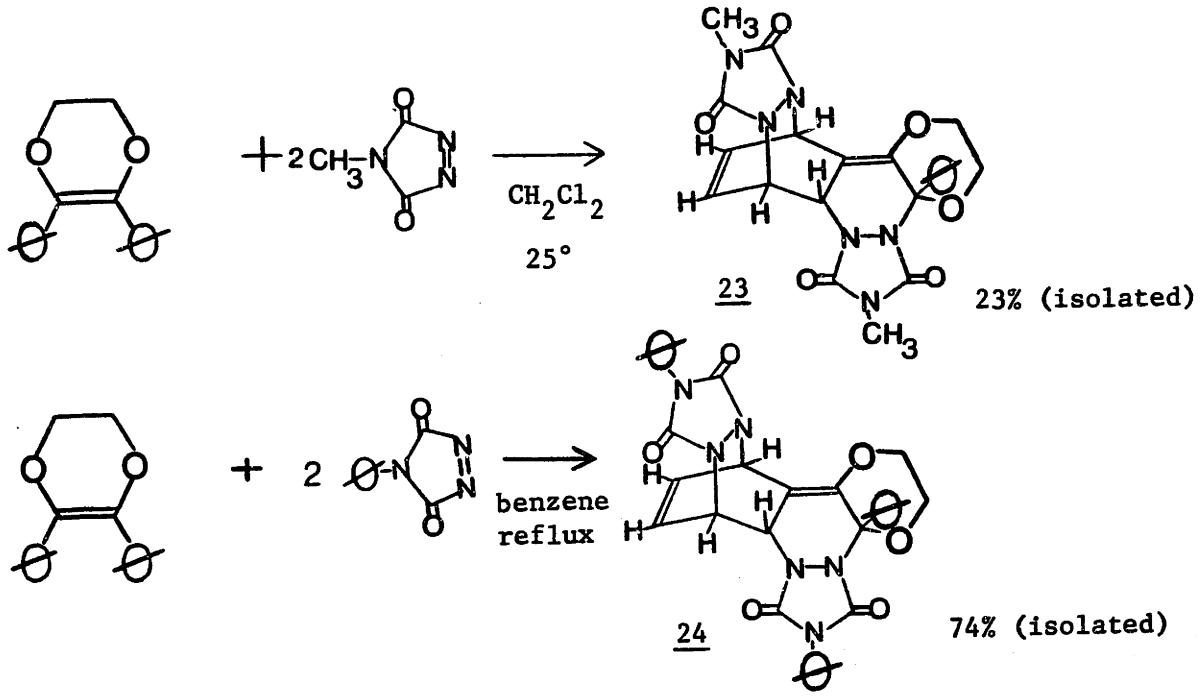
22 21

42% 58%

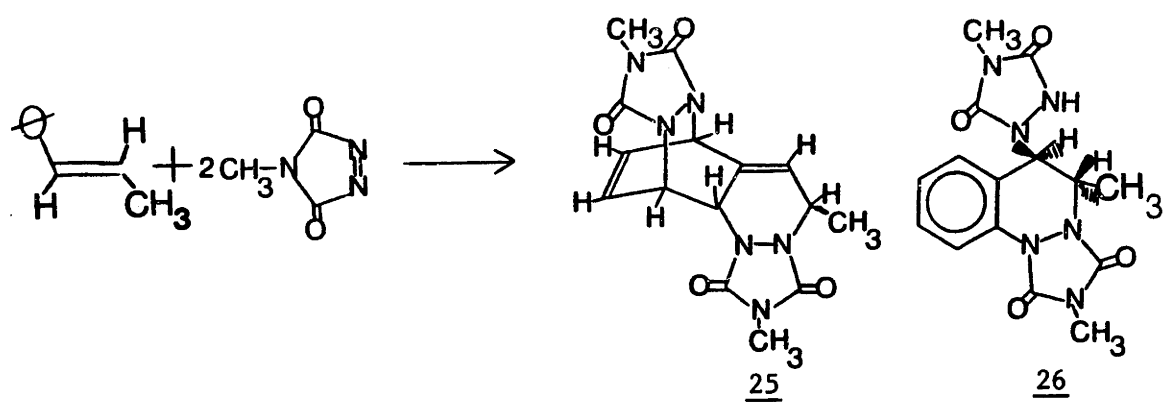
examination of the crude reaction mixture.

The reaction of 2,3-diphenyl-p-dioxene with triazolinedione was tried next in anticipation of a diazetidine product; the increased electron density of the central double bond in this olefin and the formation of a dioxetane product in its reaction with singlet oxygen[40] made it an appealing potential precursor to a phenyl-substituted diazetidine. No evidence for a diazetidine product from the reaction of TAD with 2,3-diphenyl-p-dioxene was found; the reaction proceeded with 2:1 stoichiometry. Reaction of two equivalents N-methyltriazolinedione with 2,3-diphenyl-p-dioxene in methylene chloride at room temperature gave 23% of the Diels-Alder-Diels-Alder adduct 23.

N-Phenyltriazolinedione and the dioxene in refluxing benzene gave 74% of the corresponding double Diels-Alder adduct 24.



N-Methyltriazolinedione (two equivalents) was allowed to react with trans-1-phenylpropene to determine if ene reaction in the allylic position competes with Diels-Alder reaction. Reaction in methylene chloride was found to give only products derived from initial Diels-Alder addition, 2:1 adducts 25 (26%) and 26 (55%). "Ene" product (from



25

26%

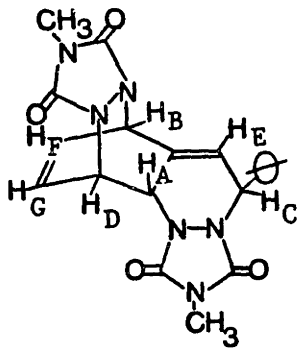
26

55%

initial reaction at the methyl group of trans-1-phenylpropene) could not be detected in crude mixtures or isolated.

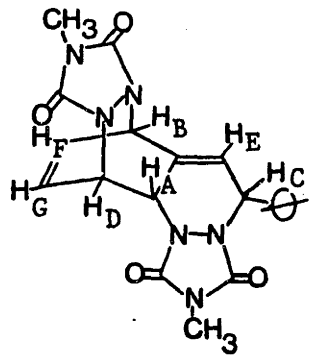
Reactions of some dienophiles with vinyl arenes have recently been reviewed.[41] Triazolinedione does not generally undergo [2+2] cycloaddition to vinyl arenes, as the preceding discussion illustrates; rather, initial Diels-Alder reaction is found to occur, followed by another Diels-Alder reaction or ene reaction, yielding 2:1 adducts only. Solvent influences the product distribution, but a pronounced solvent effect is not clear. Generally, the second ene reaction appears to be favored most in methylene chloride solvent, although no ene product was detected in the reaction of cis stilbene with TAD. Products from the

Table I. NMR Spectral Data for 2:1 Adducts of N-Methyltriazolinedione and Vinyl Arenes.



15a

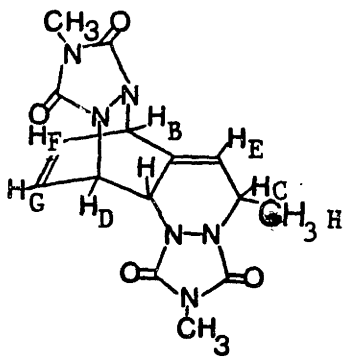
	2.87 (s,3H)
	2.89 (s,3H)
A	4.45 ("q",1H)
B	5.44 (d/d,1H)
C	5.48 (d/d,1H)
D	6.06 (quint,1H)
E	6.33 (d/d,1H)
F,G	6.65 (t,cplx,2H)
	7.35 (m,cplx,5H)
J_{DG}	=5.2
J_{DF}	=2.2
J_{BF}	=4.6
J_{BG}	=1.9
J_{DA}	=1.8
J_{EC}	=4.3
J_{AE}	=2.4
J_{AC}	=1.7



17

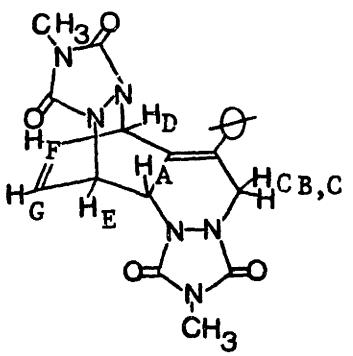
	2.90 (s,3H)
	2.93 (s,3H)
A	4.23 ("q",1H)
B	5.49 (d/d,1H)
C	5.68 (t,1H)
D	5.97 (d/t,1H)
E	6.28 (t,1H)
F,G	6.74 (t,cplx,2H)
	7.30 (m,cplx,5H)
J_{DG}	= 5.8
J_{DF}	= 1.8
J_{BF}	= 5.3
J_{BG}	= 1.7
J_{DA}	= 1.6
J_{CE}	= 2.9
J_{AE}	= 2.4
J_{AC}	= 2.4

Table I, continued.



25

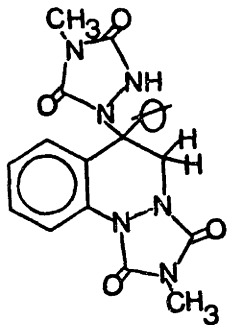
	2.86
	2.93
A	4.07 ("q",1H)
B	5.42 (d/d,1H)
C	4.60 (d/t,1H)
D	5.90 (d/t,1H)
E	6.21 (t,1H)
F,G	6.68 (t,cplx,2H)
H	1.13 (d,3H,J=6.7)
J_{BG}=	2.4 (est. from splitting)
J_{BF}=	6
J_{CE}=	2.9
J_{CA}=	2.4
J_{HE}=	6.7
J_{AE}=	2.4
J_{AD}=	1.6
J_{DG}=	5.8
J_{DF}=	1.5



21

	2.84 (s,3H)
	2.96 (s,3H)
A	4.27 (m,1H)
B,C	4.57 (2H,AB pattern,
	4.30 J= 2.2,17)
D	5.29 (1H,d/d,J=5.2 ,2.1)
E	6.03 (1H,d/t)
F,G	6.64 (t,cplx,2H)
	7.46 (m,cplx,5H)

Table I, continued.



22

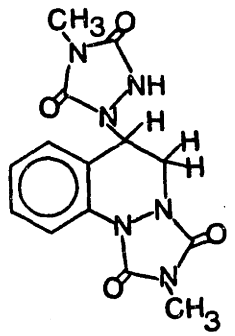
2.97 (s,3H)

2.88 (s,3H)

4.40 (d,J=12.8, AB quartet 2H)
5.12

6.80-7.49 (m,8H)

8.20 (d,J=8.5,1H)



20a

2.91 (s,3H)

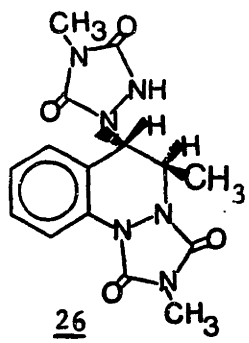
3.02 (s,3H)

3.94 (quartet of doublets, AB 2H,
4.16 J=12.9,3.7)

5.52 (t, J=3.7

7.11-7.48 (m,4H)

8.23 (d, J=8.4)



26

1.12 (d,J=6.1)

2.90 (s,3H)

3.04 (s,3H)

4.65 q/d,1H)

5.32 (d,J=1.9)

7.52-7.54(3H,aryl)

8.28 (d,J=8.6)

triazolinedione-phenylethylene reactions were isolated and fully characterized by 250 or 270 MHz NMR, using off-resonance decoupling techniques. Assignments and coupling constants for these products are listed in Table I.

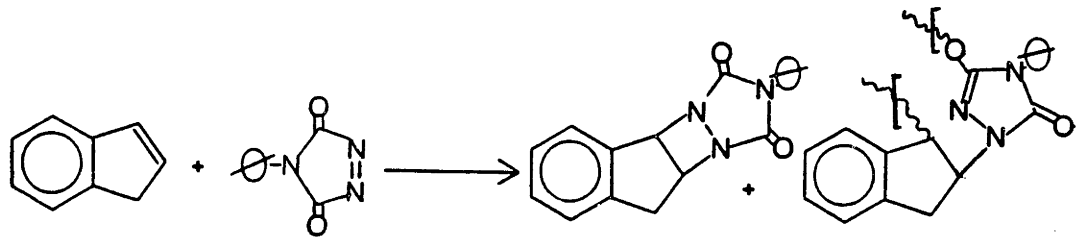
Some relative rates of reaction of the phenylethylenes toward TAD were determined (Table II). Overall, the effects are small; the observed order of reactivity is styrene > 1,1-diphenyl-ethylene > cis stilbene > trans stilbene. Reaction proceeding via full or partial charge at carbon might be expected to show rate enhancement for 1,1-diphenylethylene relative to the other phenylethylenes. The reaction of 1,1-diphenylethylene was only four times faster than the reaction of cis stilbene toward N-methyltriazolinedione.

The effects of reaction conditions on the yield of [2+2] adduct from the reaction of N-phenyltriazolinedione with indene was examined in order to maximize the yield of this useful cycloaddition (Table XI). Although indene is a vinyl arene, the product of [4+2] cycloaddition of the dienophile was not observed, probably because of the additional strain that would be involved. Reaction of indene with N-phenyltriazolinedione in benzene at 5° gives a 34% yield of diazetidine 27. Higher yields of 27 can be obtained by using lower reaction temperatures in methylene chloride or acetonitrile solvent; reaction in methylene chloride affords 27 in 69% yield. Reaction of N-phenyltriazolinedione

Table II. Relative Rates of Reactions of Phenylethylenes Toward N-Methyl triazolinedione.[1]

Olefin Pair	Relative Rate
Cis stilbene Trans stilbene	1.2
Styrene 1,1-Diphenylethylene	2.6
1,1-Diphenylethylene Cis stilbene	4.5

[1] $CDCl_3$ solvent, 25°.



with indene in the presence of 4,4'-thiobis (6-tert-butyl)-3-methyl phenol, effective in suppressing free radical side reactions in some MCPBA oxidations,[42] gave essentially the same result as reaction in its absence.

The product accompanying diazetidine 27 from the reaction of indene with N-phenyltriazolinedione drew our attention. This product had an NMR spectrum with broad absorbances around 7 ppm and at 3 to 4 ppm and had a small singlet at 2.45 ppm. The IR spectrum had carbonyl stretches at 1770 and 1715 cm^{-1}. The compound is considered to be polymeric (structure 28), largely on the basis of the broad bands in the NMR spectrum.

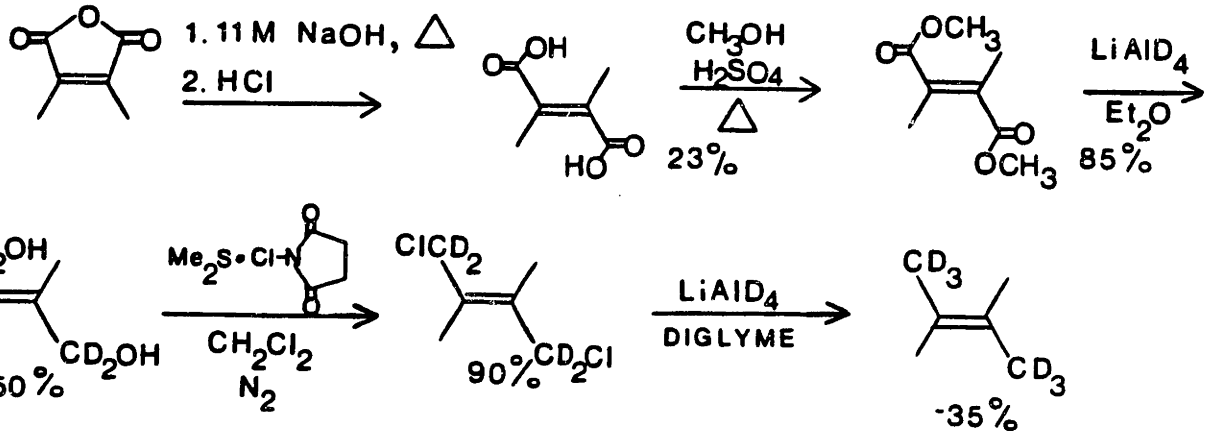
II. Mechanisms of the Ene Reaction

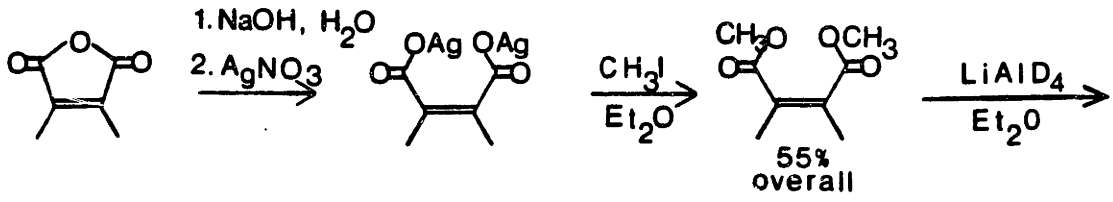
Mechanism of the Ene Reaction of Triazolinedione with Olefins

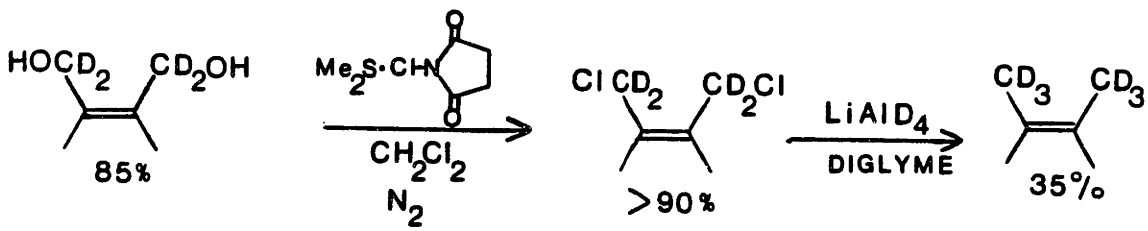
Generally, the ene reaction has not been extensively investigated from a mechanistic standpoint; the details of these mechanisms are currently a topic of considerable interest. Triazolinediones are electron-deficient cis-locked azo enophiles whose reactions with olefins are of synthetic and mechanistic interest. Some proposals have been made for TAD reactions. A concerted mechanism has been suggested for reaction with olefins on the basis of absence of substantial solvent effects.[27a] Reactions of TAD with vinyl ethers have been described as stepwise, proceeding via a 1,4-dipolar intermediate on the basis of an internal trapping experiment.[26]

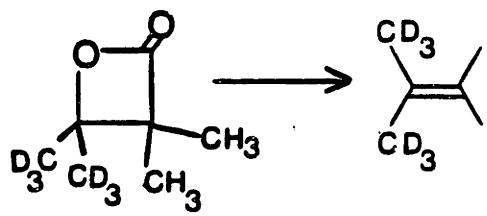
TAD and singlet oxygen show several similarities in their reactions: both react with dienes in Diels-Alder fashion, with some olefins in [2+2] fashion, and with olefins possessing allylic hydrogen in ene reactions. Stephenson has devised an interesting test concerning ene reactions by use of cis and trans d_6-deuterated tetramethylethylenes.[23,24] His studies of singlet oxygen with these olefins provide strong evidence for a perepoxide intermediate (or an intermediate with the structural characteristics of a perepoxide).

We have applied the Stephenson isotope test to the reaction of triazolinedione with 2,3-diemthyl-2-butene, using cis, trans, and gem hexadeuterio-2,3-dimethyl-2-butene. The syntheses of the cis and trans, and gem hexadeuterioolefins are summarized below.


1. 11 M NaOH, △
2. HCl
CH3OH
H2SO4
△
23%
LiAlD4
Et2O
85%
CD2OH
CD2OH
50%
Me2S•Cl-N
CH2Cl2
N2
ClCD2
90%
CD2Cl
LiAlD4
DIGLYME
CD3
CD3
-35%


1. NaOH, H2O
2. AgNO3
OAg OAg
CH3I
Et2O
CH3O OCH3
55%
overall
LiAlD4
Et2O

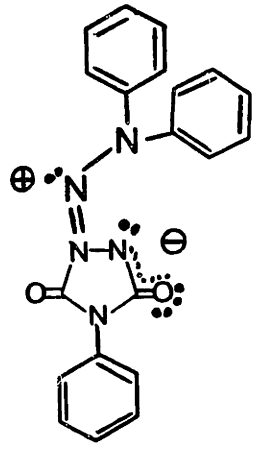

HOCD2 CD2OH
85%
Me2S•CH
CH2Cl2
N2
ClCD2 CD2Cl
>90%
LiAlD4
DIGLYME
CD3 CD3
35%


CH3
D3C CD3 CH3
CD3
CD3

Each of the deuterioolefins was reacted with N-methyl and N-phenyltriazolinedione (illustrated in the Introduction; only ene products are formed in this reaction). The resulting mixture of products, reflecting a kinetic isotope effect k_H/k_D, was analyzed by 250 MHz NMR. Reaction with cis-d_6 2,3-dimethyl-2-butene resulted in a kinetic isotope effect k_H/k_D of 1.08 ± 0.1 in the case of N-methyltriazolinedione and 1.1 in the case of N-phenyltriazolinedione. Reaction of TAD with trans-d_6 2,3-dimethyl-2-butene gave rise to a kinetic isotope effect of 3.8 ± 0.2 in the case of N-methyltriazolinedione and 3.7 in the case of N-phenyltriazolinedione. Gem-d_6 2,3-dimethyl-2-butene was allowed to react with TAD. Isotope effects of 5.70 and 5.6 were found for N-methyltriazolinedione and N-phenyltriazolinedione, respectively.

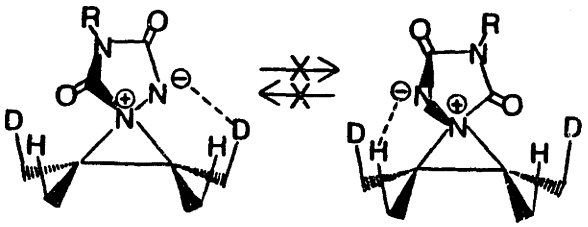
The substantial difference in isotope effects from reaction of TAD with the cis-d_6 tetramethylethylene and its trans-d_6 isomer is compelling evidence for the rate-determining formation of an intermediate in which little C-H or C-D bond breaking has taken place and whose geometry does not allow competition across the double bond. A substantial primary kinetic isotope effect from reaction of the cis-d_6 olefin with TAD would indicate either reversal of addition of TAD to olefin and the involvement of a steric isotope effect, or a mechanism in which addition of TAD to the double bond is not rate determining.

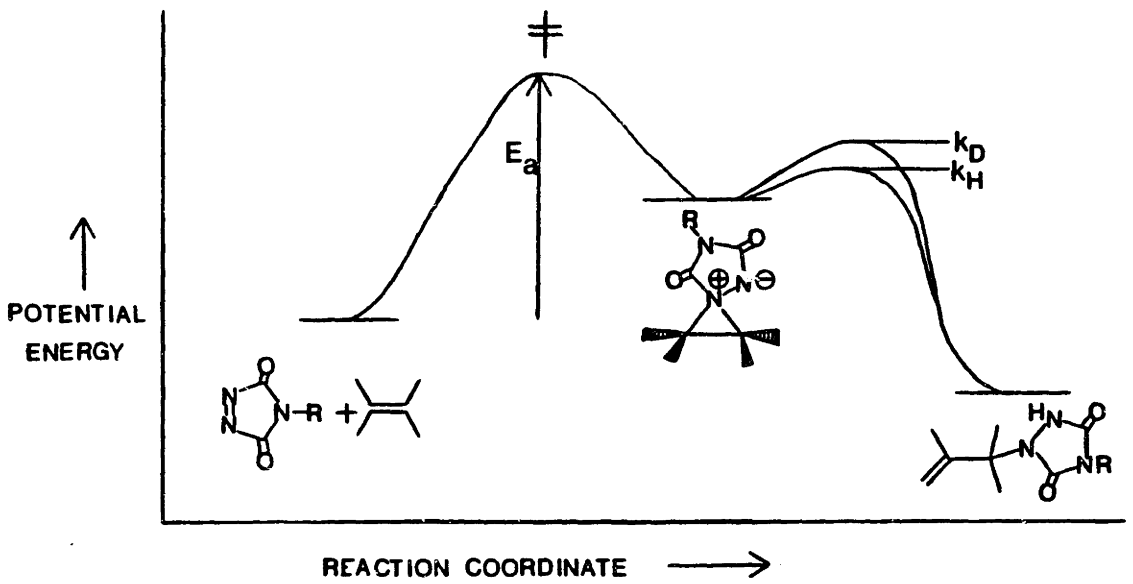
An intermediate which provides a rational basis to account for the observed isotope effects is an aziridinium imide. Such a structure has some precedence in 1-(diphenylhydrazono)-3,5-dioxo-4-phenyl-1,2,4-triazolidinium hydroxide, inner salt,[43] an insoluble zwitterionic compound.



The isotope effects of 5.62 and 5.7 obtained by reaction of TAD with the gem-d_6 olefin are unexpectedly larger than those from <u>trans</u>-TME_{d_6}. However, they are also consistent with the formation of an aziridinium imide. The larger size of these isotope effects compared to those from the <u>trans</u> olefin is discussed in conjunction with our studies on the mechanism of nitroso compound-olefin ene reactions.

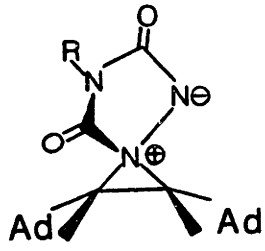
Ene reaction of triazolinedione to 2,3-dimethyl-2-butene has thus been shown to proceed in a stepwise manner. Addition of the azo compound to the olefin is rate determining, forming an intermediate for which the structure of an aziridinium imide is suggested. In a subsequent step, C-H bond breaking occurs; isotopic discrimination occurs on only one side of the double bond. Conversion to ene product is more rapid than reversion to starting material (or isomerization of the aziridinium imide). The first-formed transition state must be of higher energy than the second; otherwise, reversal of intermediate to reactants would occur with the overall result of both <u>cis</u>- and <u>trans</u>-TME-d_6 showing comparable isotope effects. This conclusion also applies to the singlet oxygen-TME reaction, i.e., perepoxide formation is rate-determining.



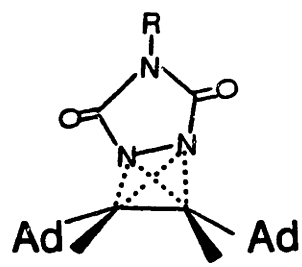

POTENTIAL
ENERGY
REACTION COORDINATE
E_a
k_D
k_H

The ene reactions of triazolinedione with olefins differ from those of dimethyl azodicarboxylate (DMAD) with olefins. For the reaction of DMAD with (S)-cis-1-deuterio-1-phenyl-4-methyl-2-pentene, the product is the S enantiomer and an isotope effect of 3 was found.[44] Consequently, the DMAD-olefin reaction was described in terms of a [4+2] transition state. In this reaction , hydrogen abstraction is involved in the rate-limiting step.

The test for the geometry of approach of triazolinedione to a double bond is provided by the reaction of TAD with an olefin like adamantylideneadamantane. A thermally allowed pathway for [2+2] cycloaddition involves anatarafacial appraoch; i.e., approach in perpendicular planes. For the TAD-adamantylidene-adamantane reaction, approach in parallel planes is not likely for steric reasons. The possibility for TAD to react in a [2+2] manner by way of an aziridinium imide was considered. Indeed, such a species was considered as a possible product of this reaction in analogy to the bromonium bromide obtained from the reaction of Br_2 with this olefin.[45]



Adamantylideneadamantane was synthesized from adamantanone with $TiCl_3$/Li and $TiCl_3$/Zn-Cu couple by the methods of McMurry.[46] The former method was found to be most reliable; high yields of coupled product were obtained. N-Methyl and N-phenyltriazolinedione were allowed to react with adamantylideneadamantane. Complete reaction took place after 15 minutes in the dark to afford a 1:1 adduct in each case. The IR spectra of the adducts had carbonyl stretching frequencies at 1730 and 1675 cm^{-1}; quite low to comparison with the usual urazole carbonyl stretching frequencies of 1750 to 1780 cm^{-1} and 1700 to 1730 $cm.^{-1}$ For the N-methyl derivative 29, the ^1H NMR spectrum (250 MHz) had 6 major peaks, and the high field ^{13}C NMR spectrum had nine lines, including one line for carbonyl carbon. The carbon splittings were established by a gated decoupling experiment. The NMR data are consistent with a diazetidine; they are also consistent with an aziridinium imide if it undergoes rapid (on an NMR time scale) isomerization (e.g., via a species such as that pictured below).



The X-ray crystal structure of the adduct of N-methyltriazolinedione and adamantylideneadamantane was determined by Dr. Blount of Hoffmann-La Roche. The structure of the compound is that of a distorted diazetidine. The atomic parameters, bond lengths, and bond angles for 29 are given in Tables III, IV, and V.

The N_1-N_2 distance of the diazetidine was 1.399 Å, and the central C_{10}-C_{20} distance was 1.635 Å. The N_1-C_{10} and N_2-C_{20} distances were 1.514 Å and 1.500 Å, respectively. The diazetidine formed in this reaction is not planar. N_1 is 0.40 Å out of the plane of C_{10}, C_{20}, and N_2, and N_1 is 0.21 Å out of the plane of C_{10}, N_2, and C_1. The adamantyl

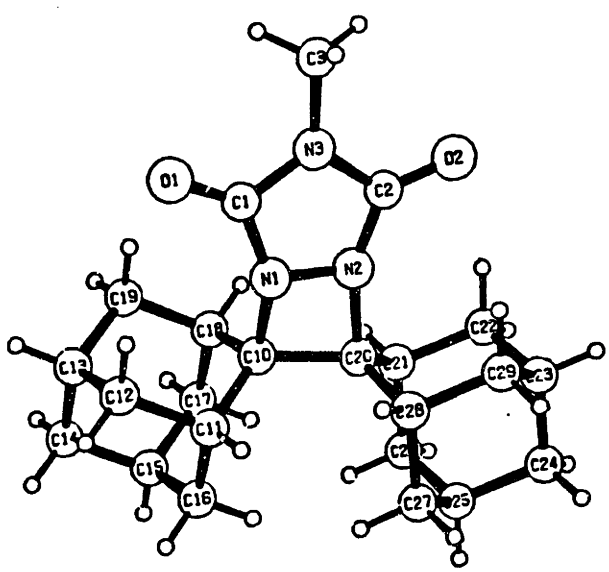


Table III. Final Atomic Parameters for 29 with Standard Deviations in Parentheses.

Atom	X	Y	Z	B
O(1)	0.7107(2)	0.6371(2)	0.0266(2)	*
O(2)	0.2821(2)	0.6387(2)	0.4462(2)	*
N(1)	0.5490(2)	0.4763(2)	0.1795(2)	*
N(2)	0.4258(2)	0.4769(2)	0.3113(2)	*
N(3)	0.4959(2)	0.6692(2)	0.2325(2)	*
C(1)	0.6033(3)	0.5961(2)	0.1319(3)	*
C(2)	0.3864(3)	0.5967(2)	0.3448(3)	*
C(3)	0.4992(3)	0.8069(2)	0.2205(3)	*
C(10)	0.5821(3)	0.3365(2)	0.2023(2)	*
C(11)	0.6127(3)	0.2637(2)	0.0759(2)	*
C(12)	0.7564(3)	0.3225(2)	-0.0464(3)	*
C(13)	0.9011(3)	0.3101(2)	-0.0122(3)	*
C(14)	0.9358(3)	0.1707(3)	0.0160(3)	*
C(15)	0.7939(3)	0.1124(2)	0.1389(3)	*
C(16)	0.6498(3)	0.1238(2)	0.1052(3)	*
C(17)	0.7620(3)	0.1829(2)	0.2682(3)	*
C(18)	0.7245(3)	0.2221(2)	0.2405(3)	*
C(19)	0.8698(3)	0.3799(2)	0.1175(3)	*
C(20)	0.4077(2)	0.3351(2)	0.3298(2)	*
C(21)	0.3834(3)	0.2749(2)	0.4737(2)	*
C(22)	0.2362(3)	0.3339(2)	0.5825(3)	*
C(23)	0.0925(3)	0.3084(2)	0.5540(3)	*
C(24)	0.0649(3)	0.1663(3)	0.5659(3)	*
C(25)	0.2094(3)	0.1052(2)	0.4584(3)	*
C(26)	0.3540(3)	0.1317(2)	0.4842(3)	*
C(27)	0.2356(3)	0.1611(3)	0.3123(3)	*
C(28)	0.2657(3)	0.3042(2)	0.2989(3)	*
C(29)	0.1188(3)	0.3649(3)	0.4080(3)	*
H(3)A	0.432	0.841	0.171	6.0
H(3)B	0.610	0.837	0.166	6.0
H(3)C	0.458	0.838	0.315	6.0
H(3)F	0.539	0.833	0.118	6.0
H(3)E	0.387	0.834	0.267	6.0
H(3)D	0.567	0.841	0.263	6.0
H(11)	0.519	0.269	0.051	3.0
H(12)A	0.776	0.278	-0.131	4.0
H(12)B	0.735	0.415	-0.064	4.0
H(13)	0.994	0.349	-0.093	4.0
H(14)A	0.956	0.124	-0.068	5.0
H(14)B	1.030	0.164	0.039	5.0
H(15)	0.815	0.020	0.158	4.0
H(16)A	0.558	0.085	0.186	4.0
H(16)B	0.669	0.077	0.022	4.0
H(17)A	0.671	0.143	0.349	5.0
H(17)B	0.857	0.178	0.290	5.0
H(18)	0.704	0.368	0.326	4.0
H(19)A	0.849	0.472	0.098	4.0
H(19)B	0.963	0.372	0.141	4.0
H(21)	0.478	0.290	0.493	3.0
H(22)A	0.219	0.296	0.678	4.0
H(22)B	0.251	0.428	0.577	4.0
H(23)	-0.002	0.349	0.624	4.0
H(24)A	-0.030	0.150	0.548	5.0
H(24)B	0.048	0.129	0.662	5.0
H(25)	0.194	0.011	0.466	4.0
H(26)A	0.447	0.091	0.414	4.0
H(26)B	0.338	0.094	0.580	4.0
H(27)A	0.140	0.146	0.295	5.0
H(27)B	0.329	0.119	0.243	5.0
H(28)	0.282	0.341	0.203	4.0
H(29)A	0.134	0.459	0.401	4.0
H(29)B	0.024	0.348	0.389	4.0

* Anisotropic thermal parameters are given in Table II

Table IV. Bond Lengths (A°) in 29 with Standard Deviations in Parentheses.

O(1)- C(1)	1.210(2)	C(14)-C(15)	1.526(3)
O(2)- C(2)	1.224(3)	C(15)-C(16)	1.519(4)
N(1)- N(2)	1.399(3)	C(15)-C(17)	1.533(4)
N(1)- C(1)	1.354(3)	C(17)-C(18)	1.526(3)
N(1)-C(10)	1.514(3)	C(18)-C(19)	1.543(3)
N(2)- C(2)	1.343(3)	C(20)-C(21)	1.520(3)
N(2)-C(20)	1.500(3)	C(20)-C(28)	1.537(4)
N(3)- C(1)	1.399(3)	C(21)-C(22)	1.541(3)
N(3)- C(2)	1.393(3)	C(21)-C(26)	1.534(3)
N(3)- C(3)	1.448(3)	C(22)-C(23)	1.523(4)
C(10)-C(11)	1.523(4)	C(23)-C(24)	1.519(4)
C(10)-C(18)	1.532(4)	C(23)-C(29)	1.525(4)
C(10)-C(20)	1.635(3)	C(24)-C(25)	1.531(3)
C(11)-C(12)	1.534(3)	C(25)-C(26)	1.519(4)
C(11)-C(16)	1.535(3)	C(25)-C(27)	1.523(4)
C(12)-C(13)	1.527(4)	C(27)-C(28)	1.531(4)
C(13)-C(14)	1.523(4)	C(28)-C(29)	1.548(3)
C(13)-C(19)	1.534(4)		

Table V. Bond Angles (°) in 29 with Standard Deviations in Parentheses.

N(2)- N(1)- C(1)	109.8(2)	C(14)-C(15)-C(17)	109.9(2)
N(2)- N(1)-C(10)	92.5(1)	C(16)-C(15)-C(17)	108.7(2)
C(1)- N(1)-C(10)	149.3(2)	C(11)-C(16)-C(15)	111.0(2)
N(1)- N(2)- C(2)	110.5(2)	C(15)-C(17)-C(18)	109.5(2)
N(1)- N(2)-C(20)	93.8(1)	C(10)-C(18)-C(17)	112.1(2)
C(2)- N(2)-C(20)	155.4(2)	C(10)-C(18)-C(19)	108.9(2)
C(1)- N(3)- C(2)	113.4(2)	C(17)-C(18)-C(19)	107.4(2)
C(1)- N(3)- C(3)	123.0(2)	C(13)-C(19)-C(18)	109.6(2)
C(2)- N(3)- C(3)	123.6(2)	N(2)-C(20)-C(10)	84.3(1)
O(1)- C(1)- N(1)	131.5(2)	N(2)-C(20)-C(21)	114.8(2)
O(1)- C(1)- N(3)	125.7(2)	N(2)-C(20)-C(28)	107.3(2)
N(1)- C(1)- N(3)	102.7(2)	C(10)-C(20)-C(21)	120.3(2)
O(2)- C(2)- N(2)	131.3(2)	C(10)-C(20)-C(28)	118.2(2)
O(2)- C(2)- N(3)	125.6(2)	C(21)-C(20)-C(28)	109.1(2)
N(2)- C(2)- N(3)	103.1(2)	C(20)-C(21)-C(22)	108.9(2)
N(1)-C(10)-C(11)	113.1(2)	C(20)-C(21)-C(26)	110.4(2)
N(1)-C(10)-C(18)	109.4(2)	C(22)-C(21)-C(26)	107.5(2)
N(1)-C(10)-C(20)	84.5(1)	C(21)-C(22)-C(23)	109.9(2)
C(11)-C(10)-C(18)	109.2(2)	C(22)-C(23)-C(24)	110.1(2)
C(11)-C(10)-C(20)	120.4(2)	C(22)-C(23)-C(29)	109.4(2)
C(18)-C(10)-C(20)	117.6(2)	C(24)-C(23)-C(29)	109.6(2)
C(10)-C(11)-C(12)	108.3(2)	C(23)-C(24)-C(25)	108.7(2)
C(10)-C(11)-C(16)	110.1(2)	C(24)-C(25)-C(26)	109.7(3)
C(12)-C(11)-C(16)	108.3(2)	C(24)-C(25)-C(27)	110.0(2)
C(11)-C(12)-C(13)	110.2(2)	C(26)-C(25)-C(27)	108.5(2)
C(12)-C(13)-C(14)	110.4(2)	C(21)-C(26)-C(25)	111.4(2)
C(12)-C(13)-C(19)	108.9(2)	C(25)-C(27)-C(28)	109.6(2)
C(14)-C(13)-C(19)	109.3(2)	C(20)-C(28)-C(27)	112.6(2)
C(13)-C(14)-C(15)	108.8(2)	C(20)-C(28)-C(29)	107.5(2)
C(14)-C(15)-C(16)	109.7(2)	C(27)-C(28)-C(29)	107.5(2)
		C(23)-C(29)-C(28)	110.1(2)

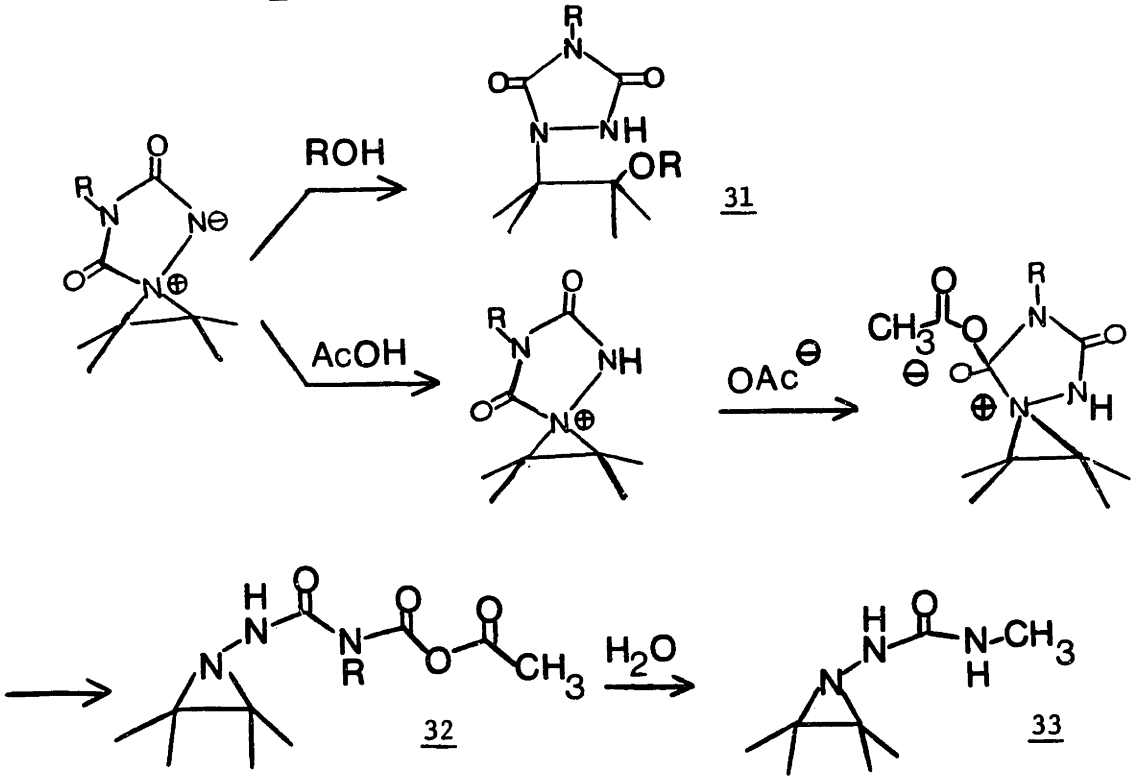
units are skewed with respect to one another; rapid interconversion between the two skewed forms accounts for the symmetry seen by NMR. The central C-C bond of this diazetidine is unusually long (1.635 Å) compared to typical $C(sp^3)$-$C(sp^3)$ bond distances of 1.53 Å. The reaction of singlet oxygen with adamantylideneadamantane has been reported to give a dioxetane of unusual stability.[47] The crystal structure of this dioxetane shows a nonplanar dioxetane ring and skewed adamantyl units. The central C-C bond in the dioxetane is 1.549 Å.[48]

The formation of the diazetidine may occur via a [2s + 2a] transition state followed by formation of an aziridinium imide, or may occur by direct formation of aziridinium imide which then collapses to give the diazetidine. These possibilities may also apply to the TAD-TME reaction.

When diazetidine 30 is refluxed in chloroform, the system undergoes reversal to adamantylideneadamantane and TAD, trapped as the ene adduct by added tetramethylethylene. Diazetidine reversal to olefin and TAD is also found in the behavior of the adducts on melting (the colorless crystals form a red melt). The diazetidine derived from indene 27 also undergoes reversal on heating; indene and the ene adduct of phenyl-TAD and TME are isolated after refluxing the diazetidine in chloroform containing TME.

Further evidence for an aziridinium imide intermediate was sought through trapping experiments. Reaction of an aziridinium imide with alcohols might result in opening of the aziridine ring to give 31. Trapping might also occur with an acid via protonation of the aziridinium

imide (the pKA of the protonated aziridinium imide is estimated to be about 10), followed by urazole hydrolysis. In the presence of water, the anhydride 32 would also be hydrolyzed to give 33.

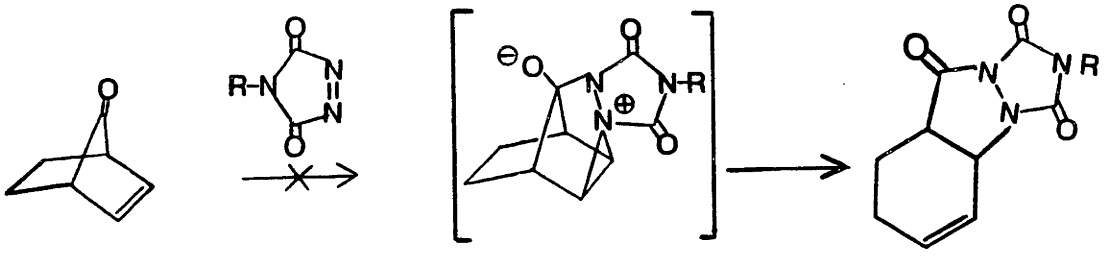


Several attempts to trap an aziridinium imide were made. Reaction of tetramethylethylene with N-methyltriazolinedione in methanol or with N-phenyltriazolinedione in methylene chloride containing methanol gave ene product only, as did reaction of TME with N-methyltriazolinedione in methylene chloride containing acetic acid. Reaction of TME with N-methyltriazolinedione in dioxane containing p-toluenesulfonic acid failed to give any of the anticipated trapping products. Trapping of an intermediate was also attempted from the adamantylideneadamantane-TAD reaction in both the forward and reverse directions. Reaction of adamantylideneadamantane with N-methyltriazolinedione in methanol gave

the diazetidine, as did reaction of the olefin with N-methyltriazolinedione in dioxane containing TsOH·H_2O or in dioxane-methylene chloride containing TsOH H_2O or in dioxane-methylene chloride containing TsOH H_2O. From the reverse direction heating the diazetidine 30 in methanol containing TME gave adamantylideneadamantane and no evidence of products of attack on an aziridinium imide.

Reaction of diazetidine 30 with TsOH H_2O in water and dioxane containing TME also only afforded products of full reversal to olefin and TAD. Refluxing the diazetidine in methanol gave adamantylideneadamantane.

It was also expected that an aziridinium imide might be trapped internally by addition of triazolinedione to 7-norbornenone.



Stirring N-methyltriazolinedione with norbornenone in deuteriochloroform at room temperature for 48 hr gave only decomposition products of triazolinedione and unreacted ketone. Stirring N-phenyltriazolinedione in deuteriochloroform or benzene containing the ketone under argon for 2 days gave only unreacted ketone and decomposition products of TAD. Competition reaction of TAD with norbornene and

norbornenone in deuteriochloroform for 8 hr at room temperature gave products from reaction of TAD with norbornene only.

We were also interested in the possibility of diazetidine formation from reaction of triazolinedione with norbornylidene-norbornane. The steric requirements for additions to this olefin differ slightly from those for addition to adamantylideneadamantane. In contrast to adamantylideneadamantane, which forms a stable bromonium bromide on reaction with bromine, norbornylidenenorbornane reacts with bromine to give a dibromide.[49]

7,7-Dimethyoxybicyclo-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene was reduced with sodium in THF by a modification of the method of Gassman[50] to give 7,7,-dimethoxybicyclo[2.2.1]hept-2-ene in 44% yield. Hydrogenation with Pd/C in a Parr apparatus afforded 7,7-dimethoxybicyclo[2.2.1]heptane. Hydrolysis with glacial acetic acid gave 7-norbornanone in 74% yield. Coupling with $TiCl_3$/Li afforded norbornylidenenorbornane in 43% yield.

Reaction of norbornylidenenorbornane with N-methyl or N-phenyltriazolinedione gave 1:1 adducts. The IR spectra of the compounds had carbonyl stretches at 1750 to 1760 cm^{-1} and 1700 cm^{-1}, higher in frequency than those for the diazetidines from adamantylideneadamantane, but lower than those of other urazoles. The ^1H NMR and ^{13}C NMR spectra are consistent with the diazetidine products. The products are therefore assigned diazetidine structures; it is expected that the diazetidine units in these adducts are more nearly planar than those from adamantylidene adamantane, accounting for the higher carbonyl stretching frequencies. The reaction of TAD with norbornylidenenorbornane is slower than the reaction with adamantylideneadamantane; complete reaction took place in

ca. 45 minutes in this case.

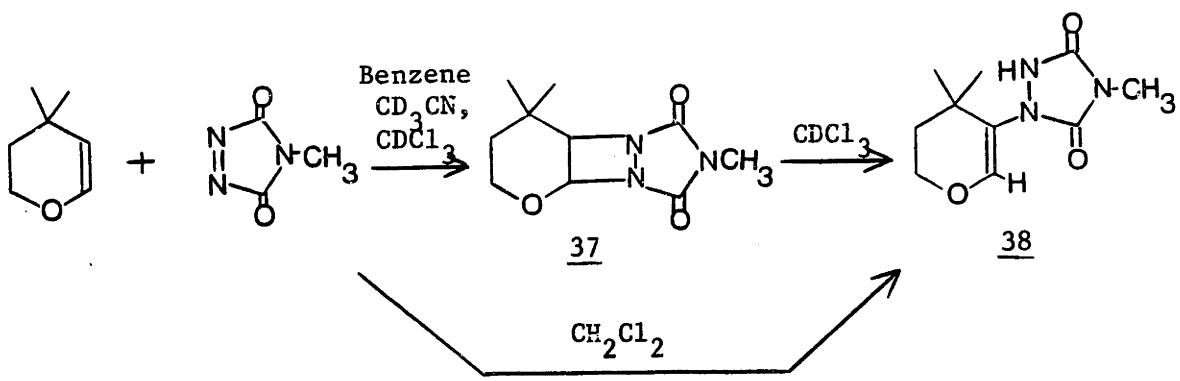
The relative rates of ene reaction of N-methyltriazolinedione with tetramethylethylene and Diels-Alder reaction of N-methyltriazolinedione with 1,3-cyclohexadiene were measured. In methylene chloride solvent, MeTAD is 30 times more reactive in the Diels-Alder reaction with 1,3-cyclohexadiene than in the ene reaction with tetramethylethylene. In benzene, this ratio is approximately 100. The threefold relative enhancement of the ene reaction in the more polar solvent is consistent with an ene transition state more polar than that of the Diels-Alder reaction of TAD with 1,3-cyclohexadiene.

Reaction of TAD with 2,3-dimethyl-2-butene had thus been shown to proceed by a mechanism in which there is rate-determining addition of TAD to the olefin, followed by formation of an intermediate (for which an aziridinium imide is suggested) after which allylic C-H abstraction occurs. Approach of TAD to olefin can occur in perpendicular planes; this type of approach precedes diazetidine formation. Reactions of TAD with olefins may generally proceed <u>via</u> an aziridinium imide; the aziridinium moiety of such an intermediate need not always be symmetrical with respect to the two ring C-H bonds. The reaction of TAD with indene can be explained in terms of an unsymmetrical species. The aziridinium imide formed can be stabilized by a partial charge at the benzylic carbon; the C-N bond to that carbon may be more ionic than the other C-N bond. Ene reaction from such a structure would require the unfavorable process of breaking the stronger C-N bond of the aziridinium imide.

Reaction of Triazolinedione with 4,4-Dimethyl-2,3-Dihydropyran

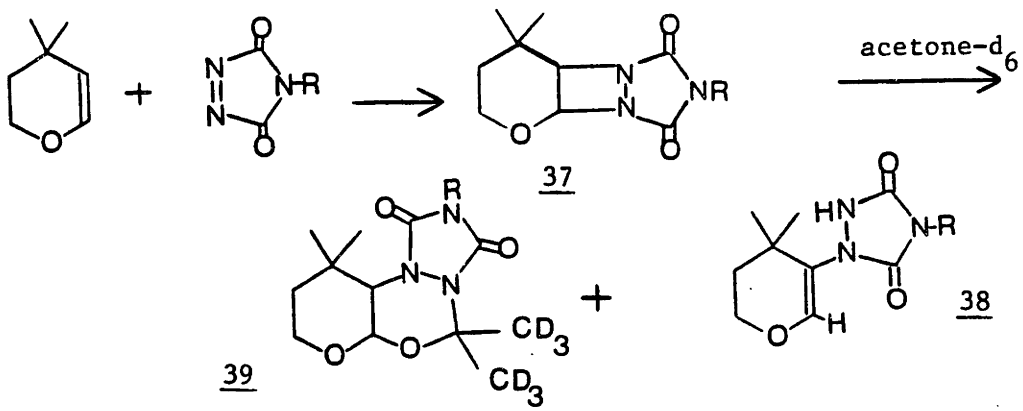
There are reports that triazolinediones react with vinyl ethers to give diazetidines and polymeric products, attributed to a 1,4-dipolar intermediate.[26] In acetone solvent, Butler[26a] has isolated oxadiazines, and has ascribed these to reaction of acetone with a 1,4-dipolar intermediate. In view of our interest in stable diazetidines as potential diazetine precursors, the reaction of TAD with 4,4-dimethyl-2,3-dihydropyran was investigated.

N-Methyltriazolinedione was allowed to react with 4,4-dimethyl-2,3-dihydropyran in deuteriochloroform while following the reaction by NMR. Initially, a diazetidine product was formed which isomerized to vinyl urazole 38. Reaction in methylene chloride solvent gave quantitative conversion to the vinyl urazole 38. From reaction of N-methyltriazolinedione with 4,4-dimethyl-2,3-dihydropyran in benzene, the diazetidine 37 precipitated in 45% yield.



37 38

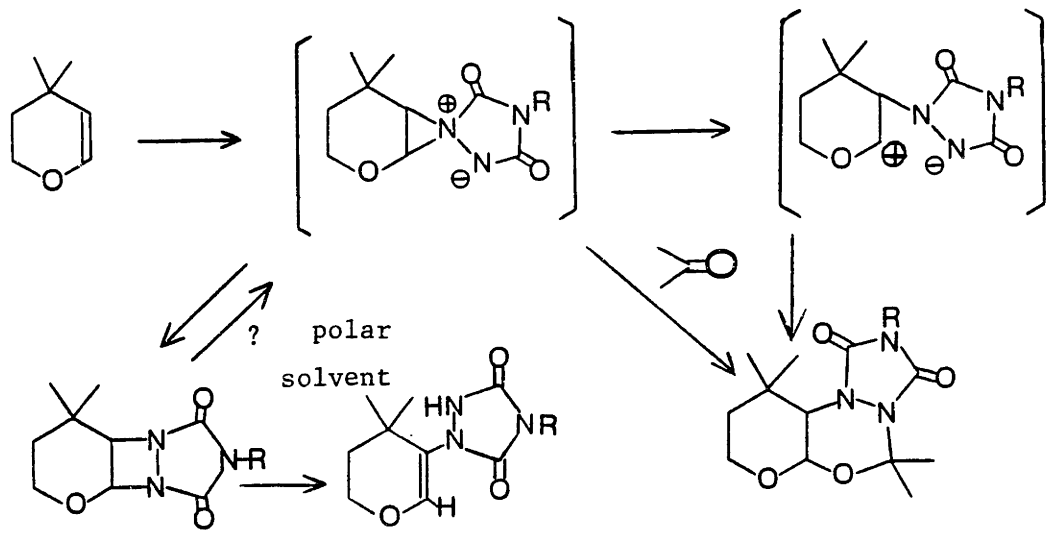
Reaction of the pyran derivative and MeTAD was also examined in acetone-d_6. After 10 minutes, the major product was diazetidine. Upon standing for 1-1/2 hrs, the diazetidine was transformed to the oxadiazine 39 (major product) and the vinyl urazole 38. The ratio of 39 to 37 to 38 was 4:2:1. After 3 hours, only oxadiazine and vinyl urazole were present (8:1 ratio).



The reactivity of N-phenyltriazolinedine toward the pyran is similar to that of N-methyltriazoline dione; reaction in benzene gave 65% of diazetidine 37. Reaction of N-phenylTAD with the pyran in deuterioacetonitrile was followed by NMR and was found to give the diazetidine, which isomerized to the vinyl urazole in the presence or absence of acetone-d_6. This isomerization is slower in deuterioacetonitrile than in deuteriochloroform, possibly catalyzed by acid.

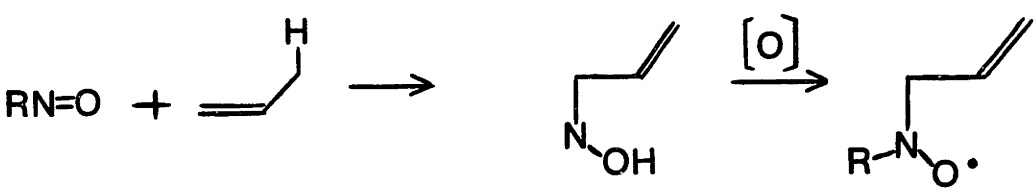
The formation of diazetidine from the pyran and TAD in nonpolar solvents means that a 1,4-dipolar species is not a necessary intermediate in this first step. One sees, however, that the diazetidine is easily transformed in polar media to products involving C-N cleavage. The vinyl urazole and the acetone-trapping product, oxadiazine, may be derived from conversion of the diazetidine to an aziridinium imide

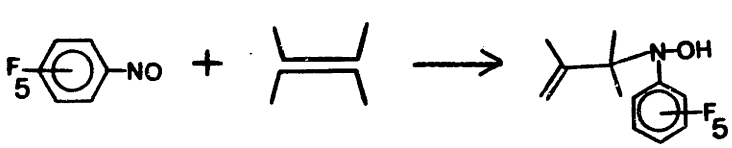
and/or a 1,4-dipolar species.



Mechanisms of the Ene Reaction of Pentafluoronitrosobenzene and N,N'Bis-(p-toluenesulfonyl) Sulfur Diimide with 2,3-Dimethyl-2-butene

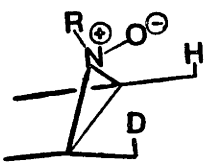
A secondary focus of our studies on mechanisms of the ene reaction involves investigation of other heteroatom enophiles in order to determine how broadly the three-center intermediate pattern applies in reactions of olefins with various reagents. Nitroso compounds generally react with olefins to give products from simple ene reaction or a paramagnetic species derived from the ene products by oxidation. The formation of the latter product complicates mechanistic study of these reactions by NMR. Pentafluoronitrosobenzene, however, reacts with tetramethylethylene quantitatively in the ene reaction to give a hydroxylamine of moderate stability.[29] We have studied the reaction of pentafluoronitrosobenzene with 2,3-dimethyl-2-butene employing the Stephenson isotope test.

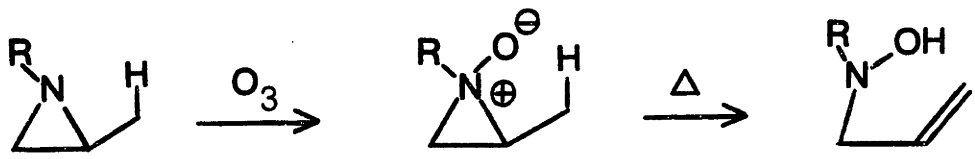




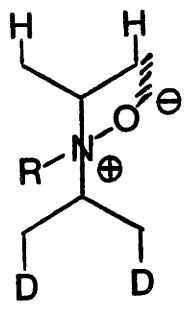
Cis, trans, and gem-d_6 tetramethylethylene were reacted with pentafluoronitrosobenzene (obtained by oxidation of pentafluoroaniline with Caro's acid or MCPBA); kinetic isotope effects were measured by NMR. An isotope effect of 1.2 ± 0.1 was found for reaction with cis-TME-d_6. Reaction with the trans olefin gave an isotope effect of 3.0 ± 0.1, and reaction with the gem olefin gave an isotope effect of 4.5 ± 0.1. The size of the isotope effects for the isomeric d_6-olefins generally parallels the findings for the reaction of these olefins with triazolinedione. The large difference in isotope effects between the cis and trans olefin is strong evidence in support of a mechanism involving rate-determining formation of an intermediate. C-H bond breakage occurs in a subsequent and faster step, and C-H vs. C-D competition is found only when an allylic C-H is cis to an allylic C-D.

These isotope effects are accommodated by an aziridine N-oxide intermediate. Aziridine N-oxides have been postulated as intermediates in the ozonolysis of aziridines at low temperature; they decompose to hydroxylamines on warming.[28]

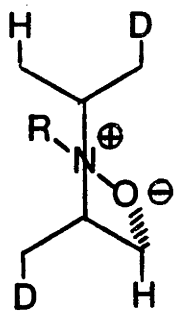




The difference in size of isotope effects between the trans-d_6 olefin and gem-d_6 olefin requires comment. Conversion of aziridine N-oxide to olefin may involve twisting (see figure, below). In the case of the gem-d_6 olefin, for C-H cleavage by the oxygen, such twisting would place the C_6F_5 group near a CD_3 group (smaller than CH_3), while C-D cleavage places C_6F_5 near to a CH_3 group. In the trans TME-d_6 case, these steric effects are reversed, in accord with a lower value for the isotope effect in the C-H vs. C-D abstraction reaction.



Gem-d_6

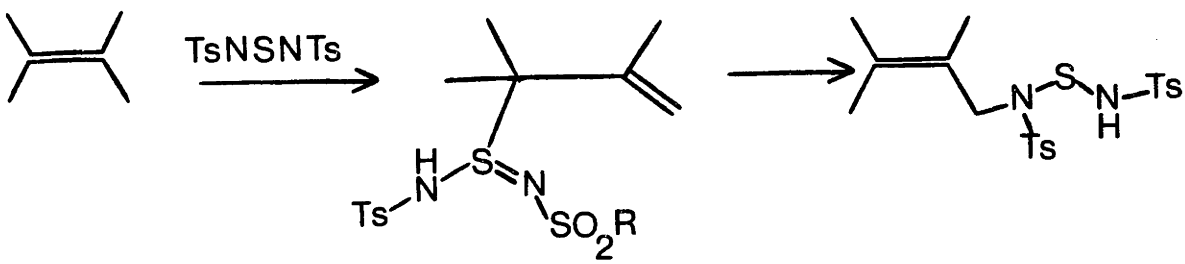


Trans-d_6

The hyperconjugative effect may also favor the formation of H abstraction product from the gem olefin intermediate (six hyperconjugating C-H's) to a greater extent than for the trans olefin intermediate (three hyperconjugating C-H's). These considerations are also applicable to the difference in isotope effects found for the reaction of triazolinediones with gem-d_6 and trans-d_6 2,3-dimethyl-2-butane.

On the basis of these isotope effects the mechanism of ene reaction of pentafluoronitrosobenzene with 2,3-dimethyl-2-butene is best described by a three-center intermediate, an aziridine N-oxide, similar in geometry to a perepoxide or an aziridinium imide.

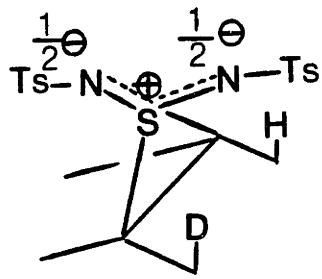
As a further exploration of the generality of the occurrence of three-center intermediates in the reactions of heteroatomic enophiles with olefins, the reaction of bis N,N'-p-toluenesulfonyl sulfur diimide with 2,3-dimethyl-2-butene was studied. The compound, obtained by reaction of N-sulfinyl-p-toluenesulfonamide with pyridine in benzene, reacts quantitatively with olefins in an ene reaction. In the case of tetramethylethylene, the ene product undergoes a [2,3] sigmatropic rearrangement to give the final product.



The intramolecular isotope effects from cis, trans, and gem-d_6 2,3-dimethyl-2-butene were measured by NMR and were found to be 3.9 ± 0.5 , 3.2 ± 0.5 , and 4.9 ± 0.4 , respectively. In an intermolecular isotope effect experiment, a 1:1:1 mixture of bis N,N'-p-toluenesulfonyl sulfur diimide, tetramethylethylene-d_o and tetramethylethylene-d_{12} were allowed to react in diethyl ether. The relative amounts of TME-d_o and TME-d_{12} were measured at t_o and after the reaction (involving 50% consumption of the tetramethylethylene reactant) with GC/mass spectral analysis.[51] The intermolecular

isotope effect from TME-d_o and TME-d_{12} was 1.03.

The lack of an isotope effect in the intermolecular reaction, coupled with the large intramolecular isotope effects, is consistent with the formation of an intermediate in this reaction. The observation of substantial and nearly equivalent isotope effects from both the cis and trans-d_6 olefins is consistent with the formation of a three-center intermediate which differs in geometry from a perepoxide, aziridinium imide, or aziridine N-oxide in that this intermediate is symmetrical with respects to both sides of the olefin.



As in the cases involving triazolinedione and the nitroso compound, the larger isotope effect from reaction of the sulfurdiimide with TME-d_6 is somewhat unexpected. It may be due to electronic effects (hyperconjugation) and steric effects in a manner analogous to those discussed for the triazolinedione-olefin or nitroso-olefin reaction.

The intermolecular competition of tetramethylethylene-d_o and tetramethylethylene-d_{12} for reaction with N-methyl and N-phenyltriazolinedione and for pentafluoronitrosobenzene were also performed and isotope effects in these cases is further support of an intermediate

involving little change in the allylic C-H (or C-D) bonds, in agreement with the conclusions derived from the intramolecular isotope effects with the d_6-tetramethylethylenes.

EXPERIMENTAL

Melting points were taken in a Thomas-Hoover "Unimelt" and are corrected. Boiling points are uncorrected. Infrared spectra (ir) were recorded on Perkin Elmer model 237-B, 567, or 283 infrared spectrophotometers in cm^{-1} with the following notations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; br, broad. Proton nuclear magnetic resonance spectra (NMR) were recorded at 60 MHz on a Varian model T-60, or Perkin-Elmer model R-24B spectrometer, at 90 MHz on a Jeol FX-90Q Multi Nuclei NMR spectrometer, and at 250 and 270 MHz on Bruker WM 250 and WM 270 spectrometers. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained on a Jeol FX-90Q Multi Nuclei NMR Spectrometer and a Bruker WM 250 spectrometer. Signals are reported in parts per million (ppm) downfield from tetramethylsilane (organic solvents) or 2,2-dimethyl-2-silapentane-5-sulfonate (water) with the following notations: s, singlet; d, doublet; t, triplet; q, quartet; br, broad. Ultraviolet and visible spectra were determined on a Cary 14 or Perkin Elmer 330 spectrophotometer. Mass spectra were recorded at 70 eV on a Varian MAT 44 equipped with a Varian Aerograph Series 1400 gas chromatograph. GC/MS analyses were performed on a Hewlett Packard 5990-A GC/MS at 70 eV.

Elemental microanalyses were performed by Robertson Laboratory, Florham Park, New Jersey.

Analytical thin layer chromatography (TLC) was performed using "Baker-flex" silica gel 1B-F and aluminum oxide 1B-F coated plastic plates. Gas liquid partition chromatography (GLC) anlayses and

separations employed F and M 270 (thermal conductivity, helium), Varian Aerograph 200 (thermal conductivity, helium), Varian Aerograph 3700 (thermal conductivity, helium, and flame ionization) and Perkin-Elmer 3920 B (flame ionization) gas chromatographs and the following columns:

Column A: 6' x 1/4" aluminum, 15% SE-30 silicone oil on Chromasorb W.

Column B: 6' x 1/4" aluminum, 15% Carbowax 20 M on Chromasorb W.

Column C: 6m x 1/8" steel, 3% UCW-98 on Chromasorb P.

Column D: 6m x 1/8" steel, 3% cyanomethyl ethylsilicone on Chromasorb P.

Lithium aluminum deuteride (98% D) was obtained from Aldrich Chemical Company. Acetone-d_6 (Merck) was 99.5% deuterated.

Tetrahydrofuran was distilled from purple solutions of sodium benzophenone ketyl. Benzene was distilled from calcium hydride. Diethyl ether was obtained from freshly opened cans (Mallinckrodt). Petroleum ether was distilled from potassium permanganate.

2-Bromo-2-nitrobutane was prepared according to a modification of the method of Iffland and Yen.[52] N-Bromosuccinimide (102.0 g, 0.573 mol) was suspended in 400 mL water and was cooled to 0°. Sodium bicarbonate (48.2 g, 0.574 mol) and 2-butanone oxime (25.0 g, 0.287 mol) were suspended in 300 mL water; the suspension was added to the NBS mixture over 15 min. The mixture was stirred 1 hour and was extracted 5 times with 200 mL portions of pentane. The pentane solution was evaporated under reduced pressure until the volume was reduced to 150 mL. The solution was cooled with stirring to 0° and was carefully treated with 50 mL nitric acid. The mixture was stirred 12 hr, and was carefully diluted with 300 mL water. The mixture was extracted 4 times with 250 mL portions of pentane. Drying ($MgSO_4$), evaporation, and distillation gave 2-bromo-2-nitrobutane (21.9 g, 42%), as a yellow-green oil: bp 58-62° (aspirator vacuum) (lit.[52] bp 78°, 30 Torr); ir ($CHCl_3$) 2980 (s), 2940 (m), 2880 (m), 1550 (vs), 1440 (s), 1380 (s), 1340 (s), 1320 (s), 1280 (m), 1140 (m), 1130 (m), 1090 (s), 1040 (s), 1000 (w), 980 (w), 870 (m), 840 (m), 720 (m); NMR ($CDCl_3$) 1.07 (t, 3 H), 2.23 (s, 3 H), 2.43 (q, 2 H).

2-Nitrobutane was made according to a modification of the method of Iffland and Yen.[52] To a suspension of sodium borohydride (30.0 g, 0.79 mol) in 75% ethanol-water (600 mL) at 0° was added 2-bromo-2-nitrobutane (50.0 g, 0.27 mol) dropwise over 1 hr, maintaining the temperature below 10°. The mixture was allowed to warm to room temperature over 2 hr, and was stirred at room temperature 1 hr. Ethanol was removed by rotovap. The residue was dissolved in 250 mL water, cooled to 5°, and was acidified to pH 6 with hydroxylamine hydrochloride. The solution was stored in the cold 24 hr and was then saturated with NaCl. The solution was divided into four portions; each portion was extracted 3 times with 100 mL ether. The ether was dried ($MgSO_4$) and evaporated to give a yellow oil (18.2 g, 65%). The oil was distilled to give 2-nitrobutane as a clear oil: bp 37-43° (aspirator vacuum) (lit.[11d] bp 40-42°, 20 Torr); ir and NMR properties were found to be identical to those of an authentic sample.

3,4-Dimethyl-3,4-dinitrohexane. The lithium salt of 2-nitrobutane (10.5 g, 96 mmol) was suspended in 250 mL dimethylsulfoxide (freshly distilled from CaH_2); the suspension was purged with a stream of nitrogen 1 hr. 2-Bromo-2-nitrobutane (17.5 g, 96 mmol) was added by syringe under nitrogen with stirring. The mixture was stirred 12 hr in a closed flask, and was poured into 250 mL ice-water. The mixture was extracted 5 times with 100 mL portions of ether. The ether was dried ($MgSO_4$) and evaporated to give 23.3 g yellow semisolid. Recrystallization from 95% ethanol afforded a meso-dl mixture (1:1) of 3,4-dimethyl-3,4-dinitrohexane (13.8 g, 70%), as a white crystalline solid: mp 75-77° (lit.[11d] mp 77-79°); ir and NMR properties were found to be identical to those of an authentic sample.

2,3-Dihydroxylamino-2,3-dimethylbutane was synthesized by the method of Lamchen and Mittag.[32] Ammonium chloride (10.0 g, 187 mmol) and water (100 mL) were put in a 300 mL 3-necked round bottomed flask fit with an overhead stirrer and temperature bath. 2,3-Dimethyl-2,3-dinitrobutane (17.6 g, 100 mmol) was added to the mixture, forming a suspension. The mixture was cooled to -5°. Zinc dust (activated, 40.0 g, 610 mmol) was added over 1-1/2 hr with constant stirring, maintaining the temperature at -5°; the mixture was then stirred 21 hr at 0°. After warming to room temperature over 2 hr, the suspension was filtered. The filter cake was washed with water and the combined washings and filtrate were cooled to 0° and acidified to pH 1.5 with concentrated HCl. The solution was evaporated under reduced pressure until a clear syrup of the dihydrochloride salt was obtained. The crude oil was put in a beaker and cooled over ice-water. Powdered K_2CO_3 (100 g) was added. The mixture was stirred until uniform with a spatula and was divided into three portions in Sohxlet thimbles. Each portion was extracted with THF 12 hr. The solids were washed with THF and the extracts and washings were combined and dried (K_2CO_3). Evaporation under reduced pressure and drying under high vacuum (2 Torr) gave 9.84 g (66%) of an off-white solid which was found by NMR to contain acetone oxime and 2,3-dihydroxylamino-2,3-dimethylbutane (63%). Recrystallization from chloroform gave the dihydroxylamine as white needles: mp 166-168° (lit.[32] mp 157-159°); ir ($CHCl_3$) 3600 (sh), 3300 (br), 2990 (s), 1460 (m), 1390 (m), 1380 (s), 1370 (s), 1250 (m), 1150 (m); NMR ($CDCl_3$) 1.15 (s, 12 H), 5.30 (s, br, 4 H). The dihydrochloride salt had NMR (D_2O) 1.52 (s, 12 H).

3,4-Dihydroxylamino-3,4-dimethylhexane was synthesized by the method of Lamchen and Mittag.[32] Ammonium chloride (2.6 g, 49 mmol), ethanol (30 mL), and water (30 mL) were put in a 300 mL 3-necked round bottomed flask fit with an overhead stirrer and a temperature bath. 3,4-Dimethyl-3,4-dinitrohexane (1:1 meso:dl mixture, 5.0 g, 24 mmol) was added to the mixture, forming a suspension. The mixture was cooled to 0° with stirring. To the mixture was added zinc dust (activated, 9.6 g, 149 mmol) in portions over 3 hr, maintaining the temperature at 0°. The mixture was allowed to warm to room temperature over 2-1/2 hr, after which time the mixture was filtered. The filter cake was washed with ethanol; the washings and filtrate were combined, cooled to 5° and made to pH 1.5 with concentrated HCl. Ethanol and water were removed under reduced pressure to give a white grainy syrup of the dihydrochloride salt. The syrup was put in a 25 mL beaker and was cooled over ice-acetone. Finely powdered K_2CO_3 (12 g) was mixed with the solid with a spatula. The resulting solid was put in a Sohxlet thimble and extracted 24 hr with methylene chloride to give solutions of 3,4-dihydroxylamino-3,4-dimethylhexane.

Table VI. Oxidations of 2,3-Dihydroxylamino-2,3-dimethylbutane from Solutions of the Dihydrochloride Salt.

Oxidant	Equiv.[a]	Conditions	Products	Characterization
Br_2 Na_2CO_3	1.7-2.3 2-3.4	0° or 35°[b]	Azo dioxide, ca. 70% yield.	Isolation; NMR
Br_2 Na_2CO_3	2 2	aq. EtOH, -50°, 2-1/2 hr	Azo dioxide, 68% (sole product)	Isolation; NMR
DMAD[d] Na_2CO_3	2 2	CH_2Cl_2-H_2O, 25°[e]	Azo dioxide and oxime (60% total) 2.3:1	Isolation; NMR
Chloranil	2	CH_2Cl_2-H_2O, 25°	Azo dioxide and oxime 0.5:1	NMR
tBuOCl Na_2CO_3	2 2	CH_2Cl_2, 0°	Azo dioxide, 63% (sole product)	Isolation; NMR

[a]Number of equivalents is based on the weight of crude 2,3-dihydroxylamino-2,3-dimethylbutane.

[b]Hydroxylamine was dissolved in water; the solution was neutralized by the addition of Na_2CO_3. Sodium carbonate (listed above) was added, followed by bromine. The products were isolated by extraction (CH_2Cl_2), drying ($MgSO_4$) and evaporation of solvent.

[c]Sodium carbonate was added to pH 7 (approx. 2 equiv.), then bromine was added.

[d]Dimethyl azodicarboxylate.

[e]The reaction mixture was poured into water before extraction with $CHCl_3$.

Table VII. Oxidations of 2,3-Dihydroxylamino-2,3-dimethylbutane.

Oxidant	Equiv.	Conditions	Products	Characterization
Br_2 Na_2CO_3	1 3.5	H_2O, 25° 1 hr	Azo dioxide, 48% (sole product)	Isolation; NMR
Br_2 Na_2CO_3	10 3.5	H_2O, 25° 1 hr	Azo dioxide, 96% (sole product)	Isolation; NMR
Br_2 Na_2CO_3	2.4 3.5	H_2O, 25° 1 hr	Azo dioxide, 94% (sole product)	Isolation; NMR
tBuOCl Na_2CO_3	10 3.5	CH_2Cl_2,25°[b] 24 hr	Azo dioxide, 86% (sole product)	Isolation; NMR
tBuOCl Na_2CO_3	2 1	CH_2Cl_2,-55°[b] 24 hr	Azo dioxide, 66% (sole product)	Isolation; NMR

[a]Products from bromine oxidations were isolated by extraction with $CHCl_3$, drying ($MgSO_4$), and evaporation of solvent.

[b]Reaction mixtures from tert-butyl hypochlorite oxidations were filtered; the filter cake was washed with methylene chloride. The filtrate and washings were combined and evaporated to give the product.

Table VIII. Oxidations of 3,4-Dihydroxylamino-3,4-dimethylhexane[a]

Oxidant	Equiv.	Conditions	Products	Characterization
Tert-butyl hypochlorite[b]	2	CH_2Cl_2[c]	Azo dioxide,29% (sole product)	Isolation;NMR
Na_2CO_3	1			
Br_2	2	H_2O, 25°[d]	Azo dioxide; oxime (1:1), azo dioxide yield 8% (isolation)	Isolation;NMR
Na_2CO_3	2			
Tert-butyl hypochlorite	2	CH_2Cl_2,25°[e]	Azo dioxide; oxime (40% total) 1.2:1	Isolation;NMR
Na_2CO_3	2			
Tert-butyl hypochlorite	2	CH_2Cl_2,-50°[e]	Azo dioxide; oxime (71% total) 2.3:1	NMR
Na_2CO_3	2			

[a]Oxidations are from solutions of the dihydrochloride salt of the dihydroxylamine unless otherwise noted.

[b]From a solution of the dihydroxylamine as the free base.

[c]Product was isolated by washing the methylene chloride solution with water; drying ($MgSO_4$), evaporation, and high vacuum.

[d]Product was isolated by extraction with methylene chloride, drying ($MgSO_4$), and evaporation of solvent.

[e]Reaction mixtures were filtered; and filter cake was washed with methylene chloride. The filtrate and washings were combined, extracted with water, and evaporated to give the product.

2,3-Dimethyl-2,3-dinitrobutane was made in 69% yield from 2-nitropropane and bromine by the method of Sayre[37] with recrystallization from tetrahydrofuran: mp 216-217° (lit.[53] mp 208-209°).

3,3,6,6-Tetramethyl-1,2-diazacyclohexene was synthesized in 30% yield from 2,5-diamino-2,5-dimethylhexane, sodium tungstate, and hydrogen peroxide by the method of Greene and Gilbert:[11a] bp 42-58° (4 Torr) (lit.[11a] bp 48-50°, 4.2 Torr).

3,4,4,4-Tetramethyldiazetine was made by the method of Greene and Gilbert:[11a] NMR ($CDCl_3$) 1.15 (s, 12 H) (lit.[11a] NMR ($CDCl_3$) 1.28 (s, 12 H).

The Synthesis of Cyclic and Acyclic Silanediamines.

The preparation of compounds containing Si-N bonds requires special precautions to ensure that hydrolysis of the bond does not occur during isolation of the product. The silanediamines are sufficiently sensitive to moisture to warrant the exclusion of air from vessels containing these compounds. Glassware used in the following reactions was oven dried (120°) and cooled under a stream of dry nitrogen or argon. The reactions were carried out under a dry nitrogen or argon atmosphere, as were all transfers or the compounds and their solutions. Distillations were generally conducted using the lowest possible temperature; overheating results in significant decreases in yield. The chlorinated silanediamines are somewhat less sensitive toward moisture and heat than their precursors. The previously described precautions were also used in their preparation.

N,N'-Di-*tert*-butyldimethylsilanediamine was synthesized according to the method of Fink.[34f] The resulting yellow oil was distilled *in vacuo* through a 10 cm Vigreux column to afford a clear oil (24 g) which was sensitive to heat and to atmospheric moisture. The purity of the oil was judged to be 87% by NMR, indicating an overall yield of 60%. N,N'-di-*tert*-butyldimethylsilanediamine: bp 50-52°, 4.6 Torr (lit.[34f] bp 63°, 12 Torr); ir ($CHCl_3$) 3380 (m), 2960 (s), 2880 (m), 1465 (s), 1400 (m), 1380 (s), 1365 (s), 1255 (s), 1220 (s), 1020 (br); NMR ($CDCl_3$) 0.07 (s, 6 H), 0.55 (s, br 2 H), 1.18 (s, 18 H). Impure fractions were further purified by redistillation. In runs where a larger amount of dichlorodimethylsilane was used, N-*tert*-butylaminodimethylsilyl chloride could be isolated by distillation as a clear oil: bp 37-38°, 2.8 Torr (lit.[34c] bp 120-121°); NMR ($CDCl_3$) 0.46 (s, 6 H), 1.23 (s, 9 H).

N-Chloro-N,N'-di-tert-butyldimethylsilanediamine. To a solution of N, N'-di-tert-butyldimethylsilanediamine (9.5 g, 47 mmol) in 35 mL dry methylene chloride, shielded from light and protected from atmospheric moisture, was added a solution of tert-butyl hypochlorite (11.3 g, 104 mmol) in 25 mL methylene chloride with stirring over 15 min. The mixture was stirred at room temperature 5.5 hr. With minimal exposure to light, most of the solvent was removed by rotovap. The resulting yellow oil was distilled in vacuo in an apparatus shielded from light to afford N-chloro-N,N'-di-tert-butyldimethylsilanediamine (8.8 g, 70%) as a yellow oil: bp 74-80°, 3.9 Torr; ir ($CHCl_3$) 3390 (m), 2965 (s), 1465 (m), 1390 (m), 1380 (s), 1365 (s), 1260 (m), 1205 (s), 1045 (m), 1020 (s), 965 (s), 930 (m), 840 (m); NMR ($CDCl_3$) 0.30 (s, 6 H), 0.60 (br, 1 H), 1.18 (s, 9 H), 1.30 (s, 9 H).

N,N'-Dichloro-N,N'-di-tert-butyldimethylsilanediamine. To a solution of N,N'-di-tert-butyldimethylsilanediamine (11.4 g, 56 mmol) in 10 mL dry methylene chloride, shielded from light and protected from atmospheric moisture, was added dropwise a solution of tert-butyl hypochlorite (55 mL, 460 mmol) in 10 mL methylene chloride with stirring over 55 min. The reaction mixture was allowed to stir 19 hr at room temperature. The solvent was removed by rotary evaporation with minimal exposure to light. The yellow oil remaining was distilled in vacuo through a 10 cm Vigreux column, shielded from light, to give N,N'-dichloro-N,N'-di-tert-butyldimethylsilanediamine (11.7 g, 76%) as a yellow oil: bp 85-94°, 2.3 Torr; ir ($CHCl_3$) 2970 (s), 1460 (s), 1390 (s), 1365 (s), 1260 (s), 1260-1190 (br), 1190 (s), 1050 (s), 970 (s), 840 (s); NMR ($CDCl_3$) 0.48 (s, 6 H), 1.32 (s, 18 H); mass spectrum 270 (M^+, 4.57).

2,2,4,4,7,7-Hexamethyl-1,3-diaza-2-silacycloheptane. To a solution of dry 2,2,5,5-tetramethylbutanediamine (Aldrich, 40 mL, 230 mmol) in 300 mL hexane (distilled from CaH_2) under a dry nitrogen atmosphere was added a soluiton of dichlorodimethylsilane (Aldrich, 13.3 mL, 110 mmol) in 65 mL dry hexane with overhead stirring over 15 min. The reaction mixture was stirred at room temperature 2.5 hr. The mixture was filtered through a medium frit glass filter and the filter cake was washed with hexane. The solvent was removed from the filtrate by rotovap, and the resulting oil was distilled in vacuo to afford 2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane (13.4 g, 61%) as a clear oil; bp 62-64°, 3.5 Torr; ir ($CHCl_3$) 3410 (m), 2960 (s), 1460 (m), 1390 (m), 1370 (s), 1335 (m), 1255 (s), 1200 (m), 1190 (m), 1145 (m), 1010 (s), 860 (s); NMR ($CDCl_3$) -0.01 (s, 6 H), 1.15 (s, 12 H), 1.50 (s, 4 H), 0.73 (br, 2 H, exch. D_2O).

Experiments using triethylamine instead of excess diamine to scavenge the HCl afforded the product in 50-60% yield.

N-Chloro-2,2,4,4,7,7-Hexamethyl-1,3-diaza-2-silacycloheptane.

To a solution of 2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane (3.30 g, 16.5 mmol) in 15 mL dry methylene chloride under a dry nitrogen atmosphere and shielded from light was added with stirring a solution of tert-butyl hypochlorite (1.9 mL, 16.5 mmol) in methylene chloride over 15 min. The reaction mixture was stirred for 6 hr more and the solvent was removed by vacuum. Short path distillation in vacuo in an apparatus shielded from light gave N-chloro-2,2,-4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane (3.0 g, 76%) as a clear yellow oil: bp 54-59°, 0.4 Torr; ir ($CHCl_3$) 3400 (m), 3020 (s), 2970 (s), 1520 (m), 1425 (m), 1380 (s), 1365 (s), 1260 (s), 1220 (s), 1140 (s), 1025 (s), 930 (s); NMR ($CDCl_3$) 0.23 (s, 6 H), 1.12 (s, 6 H), 1.23 (s, 6 H), 1.70 (s, 4 H); mass spectrum 234 (M^+, 4.81). Higher boiling fractions were found to contain N,N'-dichloro-2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane (8%).

Reaction under the above conditions but using 2.5 equivalents of tert-butyl hypochlorite (instead of 1.0) afforded N,N'-dichloro-2,2,4,4-7,7-hexamethyl-1,3-diaza-2-silacycloheptane (10.4 g, 77%) as a thick yellow oil: bp 113-118°; 3.8 Torr; ir ($CHCl_3$) 2935 (s), 1450 (m), 1385 (s), 1370 (s), 1255 (s), 1210 (s), 1180 (m), 1025 (s), 940 (m), 920 (m), 840 (m); NMR (CCl_4) 0.37 (s, 6 H), 1.20 (s, 12 H), 1.80 (s, 4 H); mass spectrum 268 (M^+, 4.58).

Chlorination of 2,2,4,4,7,7-Hexamethyl-1,3-diaza-2-silacycloheptane with N-Chlorosuccinimide. To a solution of 2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane (3.00 g, 15 mmol) in 3 mL dry carbon tetrachloride, cooled to -10°, was added with stirring under a dry nitrogen atmosphere a suspension of N-chlorosuccinimide (2.00 g, 15 mmol) in 15 mL carbon tetrachloride by cannula. The mixture was stirred 2 hr at -10° and was allowed to warm to room temperature. The mixture was filtered and the filtrate was concentrated by vacuum. Distillation *in vacuo* afforded N-chloro-2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane (2.40 g, 68%) as a yellow oil: bp 36-39°, 0.15 Torr.

2,3-Diamino-2,3-dimethylbutane was prepared by a modification of the method of Sayre.[37] In a 3 L 3-necked round bottomed flask fitted with a thermometer, overhead stirrer, and reflux condenser, 2,3-dimethyl-2,3-dinitrobutane (52.8 g, 300 mmol) was mixed with concd. HCl (450 mL). With stirring, the mixture was warmed to 50°C. Tin (20 mesh, 225 g) was added over 3 hr, maintaining the temperature between 50° and 60°. The mixture was refluxed 30 min and was adjusted to pH 14 by the cautious addition of NaOH. The mixture was then steam distilled, collecing 1500 mL of distillate. The distillate was then cooled and made basic with NaOH until a mushy oily layer separated near the surface. The layer was collected and the aqueous fraction was continuously extracted with ether. The ether was dried with K_2CO_3 and concentrated. The residue was combined with the oily layer. The oil was dried over solid KOH and the product was purified by short path distillation from CaH_2 to give 2,3-diamino-2,3-dimethylbutane (16.6 g, 48%) as a deliquescent crystalline solid that forms azeotropes with water and alcohols; mp 95-102°; ir (CCl_4) 3490 (m), 3330 (w), 2980 (s), 2880 (m), 1590 (m, br), 1465 (m), 1390 (s), 1375 (s), 1370 (s), 1150 (s, br); NMR ($CDCl_3$) 1.12 (s, 12 H),1.28 (s, 4 H) (lit.[11d] NMR ($CDCl_3$) 1.14 (s)).

2,2,4,4,5,5-Hexamethyl-1,3-diaza-2-silacyclopentane. To a solution of 2,3-diamino-2,3-dimethyl butane (5.0 g, 43 mmol) in 150 mL dry pentane under a dry nitrogen atmosphere was added triethylamine (dried over KOH and distilled from CaH_2) (12.5 mL, 88 mmol). To this solution was added dropwise a solution of dichlorodimethyl silane (5.2 mL, 43 mmol) in 50 mL dry pentane with overhead stirring over 1.5 hr. The mixture was stirred 19 hr more. The precipitate was filtered under nitrogen through a medium frit. Solvents were removed by vacuum. Distillation in vacuo afforded 2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane (3.25 g, 44%) as a clear oil that was very sensitive to heat and atmospheric moisture: bp 25-32°, 2.5 Torr; ir ($CHCl_3$) 3440 (m), 3380 (m), 2960 (s), 1580 (w), 1460 (m), 1385 (s), 1365 (s), 1265 (s), 1210 (s), 1155 (s), 1025 (s), 970 (s), 865 (s); NMR ($CDCl_3$) 0.10 (s, 6 H), 1.07 (s, 12 H). The starting diamine could be recovered by neutralization of the precipitate by aqueous hydroxide, followed by continuous ether extraction, drying with K_2CO_3, and distillation from CaH_2.

N-Chloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane.

To a solution of 2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane (2.10 g, 12 mmol) in 5 mL dry carbon tetrachloride, cooled to -10°, was added with stirring under a nitrogen atmosphere by cannula a suspension of N-chlorosuccinimide (4.88 g, 36 mmol) in 30 mL carbon tetrachloride. The mixture was stirred 22 hr at -10° and was then filtered under nitrogen. The filtrate was concentrated by vacuum. The residue was distilled in vacuo in an apparatus shielded from light to give N-chloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane (1.12 g, 45%) as a yellow oil: bp 25-30° 0.5 Torr; ir (CCl_4) 3340 (m), 2980 (s), 1390 (s), 1380 (s), 1370 (s), 1330 (s), 1260 (s, br), 1060 (s), 1040 (s), 1025 (s), 980 (s), 880 (s); NMR ($CDCl_3$) 0.20 (s, 6 H), 1.07 (br, 1 H), 1.13 (s, 6 H).

N,N'-Dichloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane.

At 0° under a dry nitrogen atmosphere shielded from light, a suspension of N-chlorosuccinimide (5.0 g, 37.4 mmol) in 75 mL carbon tetrachloride was added by cannula with stirring to a solution of 2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane (2.20 g, 12.7 mmol) in 2 mL carbon tetrachloride. The mixture was stirred at 0° for 17 hr and then was allowed to warm to room temperature. The mixture was stirred at room temperature for 8 hr more. The mixture was filtered under nitrogen and the filtrate was concentrated by vacuum. The NMR spectrum of the filtrate prior to distillation showed quantitative conversion of the starting material to the desired product. The residue was distilled *in vacuo* to afford N,N'-dichloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane (1.70 g, 55%) as a thick yellow oil: bp 70°, 0.5 Torr; ir ($CHCl_3$) 2980 (s), 1460 (m), 1390 (s), 1375 (s), 1365 (s), 1255 (s), 1160 (s), 1140 (s), 1025 (s), 985 (s), 940 (m), 880 (m); NMR ($CDCl_3$) 0.30 (s, 6 H), 1.17 (s, 12 H); NMR (DMSO-d_6) 0.27 (s, 6 H), 1.10 (s, 12 H).

Reaction of Ethylenediamine with Dichlorodimethyl Silane.

Ethylenediamine and dichlorodimethyl silane were allowed to react according to a modification of the method of Kummer and Rochow.[36] All glassware for this reaction was flame-dried. To a solution of ethylenediamine (Aldrich, distilled from CaH_2, 6.0 g, 100 mmol) in 150 mL dry hexane under a dry nitrogen atmosphere was added a solution of dichlorodimethyl silane (6.0 mL, 49 mmol) in 75 mL hexane with overhead stirring over 15 min. The reaction mixture was stirred 6 hr and was filtered under nitrogen. The filtrate was concentrated by vacuum, and vacuum distillation of the product was attempted. Heating with an oil bath to 250° (stillhead temperature 90°) at 2 Torr did not yield any distillate. The pot residue was a gummy solid, probably polymeric, which could not be identified.

Tetraethyl Ammonium Fluoride (Aldrich) was dried under vacuum (4 Torr) at 100° 12 hours.

Tetra-n-butyl Ammonium Fluoride was prepared by the method of Corey.[54] Hydrofluoric acid (48%) was added with stirring to a cooled 10% aqueous solution of tetra-n-butyl ammonium hydroxide until just below pH 7. Water was removed by evaporation under reduced pressure to give a white solid. The solid was dried by azeotropic distillation under reduced pressure using several portions of benzene-acetonitrile (1:1), affording a semisolid. High vacuum (<30°) gave a greenish grey solid. The solid was then pulverized to give a solid of lighter color. The tetra-n-butyl ammonium fluoride was stored under anhydrous conditions.

Tetra-n-butyl ammonium fluoride could be recovered from mixtures as follows: the solid was dissolved in water. Cooling the solution over ice gave the clathrate,[55] $n\text{-}Bu_4N^+F^- \cdot 32\ H_2O$ as a precipitate. The product was washed with cold water and was dissolved in acetonitrile-benzene (1:1). The solvents were removed by rotovap (<32°). Drying under high vacuum 1 hr gave a white solid which was pulverized and stored under anhydrous conditions.

Reaction of N,N'-Dichloro-2,2,4,4,7,7-hexamethyl-1,3-diaza-2-silacycloheptane with Fluoride. To a solution of N,N'-dichloro-2,2,4,4-7,7-hexamethyl-1,3-diaza-2-silacycloheptane (1.06 g, 3.9 mmol) in 4 mL dimethyl sulfoxide (distilled from CaH_2) was added tetraethylammonium fluoride (1.20 g, 8.0 mmol) in 6 mL dimethyl sulfoxide by syringe with stirring. The mixture was stirred 3 hr, protected from moisture. The mixture was poured into 15 mL water and was extracted 3 times with 20 mL portions of ether. The ether was extracted twice with 10 mL portions of water and once with 10 mL saturated aqueous NaCl. The ether was dried ($MgSO_4$) and evaporated to give a yellow liquid which precipitated a white solid (0.26 g, 48%). The NMR spectrum of the crude product contained signals at 1.50 (s), 1.28 (s), 0.30 (s), 0.27 (s), 0.17 (s) ppm ($CDCl_3$) [lit.[11a] NMR ($CDCl_3$) 1.48 (s, 4 H), 1.28 (s, 12 H)]. The ir spectrum of the crude product ($CHCl_3$) had stretches at 2970 (s), 2940 (sh), 2870 (sh), 1615 (m), 1565 (m), 1510 (m), 1470 (sh), 1460 (m), 1385 (m), 1265 (s), 1205 (m), 1050 (s), 890 (s), 865 (m) [lit.[11a] ir (CCl_4) for 3,3,6,6-tetramethyl-1,2-diazacyclohexene 2960 (s), 1565 (m), 1475 (s), 1460 (s), 1380 (s), 1360 (s), 1340 (s)]. GLC (Column A, 120°) showed the crude product to be a mixture of four compounds. 3,3,6,6-Tetramethyl-1,2-diazacyclohexene was isolated by preparative GLC (Column A, 120°): ir (CCl_4) 2970 (s), 2940 (s), 2870 (s), 1565 (m), 1470 (s), 1455 (s), 1385 (s), 1365 (s), 1345 (s), 1260 (m), 1240 (w), 1175 (s), 860 (s). The desired azo compound comprised 62% of the total volatile product peak area.

Reaction of N-Chloro-N,N'-di-tert-butyldimethylsilanediamine with Fluoride. To a solution of N-chloro-N,N'-di-tert-butyldimethylsilanediamine (1.445 g, 6.1 mmol) in 4 mL dimethyl sulfoxide, protected from moisture, was added by syringe a solution of tetraethyl ammonium fluoride (2.015 g, 13.5 mmol) and water (0.108 g, 6.0 mmol) in 5 mL dimethyl sulphoxide over 15 min. The mixture was stirred at room temperature 4 hr. The mixture was poured into 10 mL water and was extracted 4 times with 15 mL portions of ether. The ether was extracted twice with 10 mL portions of water and once with 10 mL saturated aqueous sodium chloride. The ether was dried ($MgSO_4$) and the solvent evaporated to give a yellow oil (0.48 g, 62%). The NMR spectrum of the crude product contained signals at 1.37 (s), 1.25 (s), 1.18 (s, most prominent) and 0.23 (s) ppm (CCl_4) (lit.[56] NMR (CCl_4) for 1,2-di-tert-butyldiazene 1.13 (s, 18 h); also 1.18 (s, 18 H). The ir spectrum of the crude product (CCl_4) had stretches at 2970 (s), 2910 (m), 1460 (m), 1410 (m), 1375 (m), 1370 (s), 1265 (s), 1230 (w), 1050 (s, br), 900 (w), 860 (w) (lit.[57] ir (CCl_4) for 1,2-di-tert-butyldiazene (CCl_4) 2960 (s), 1235 (s), 1210 (s). GLC (Column A, 100°) showed the crude product to be a mixture of five compounds. The first eluted peak was identified as 1,2-di-tert-butyldiazene. The azo compound was isolated by preparative GLC (Column A, 100°): NMR (CCl_4) 1.18 (s); ir (CCl_4) 2980 (s), 1460 (m), 1395 (s), 1370 (s), 1230 (s), 1205 (s).

Reaction of N,N'-Dichloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane with Fluoride. To a solution of N,N'-dichloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane (0.20 g, 0.8 mmol) in 0.5 mL dry THF at 0° under nitrogen was added a solution of tetra-n-butylammonium fluoride (0.45 g, 0.17 mmol) in 2 mL THF by syringe over 5 min. The mixture was stirred at 0° 1.5 hr. GLC (Column A) showed the product mixture to contain five compounds. The major volatile product was identified as 3,3,4,4,-tetramethyl-$\Delta^{1,2}$-diazetine by retention time and coinjection with an authentic sample at three temperatures (50°, 70°, and 90°).

3,3,4,4-tetramethyl-$\Delta^{1,2}$-diazetine was isolated by preparative GLC (Column A, 70°): ir ($CHCl_3$) 3000 (s), 2980 (s), 2930 (s), 1480 (m), 1460 (m), 1450 (m), 1390 (m), 1380 (m), 1375 (s), 1255 (s), 1220 (br), 1140 (m), 1060 (s, br) (lit.[11a] ir ($CHCl_3$) 3000 (s), 2980 (s), 2930 (s), 1480 (m), 1460 (m), 1450 (m), 1390 (m), 1380 (m), 1375 (s), 1220 (m, br), 1170 (w), 1140 (m)). The 1255 cm^{-1} stretch in the collected material is attributed to the strong Si-CH_3 stretch found in a siloxane impurity.

Other Reactions of Fluoride with N,N'-Dichloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane. To a solution of N,N'-dichloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane (0.2 mmol) in ~0.2 to ~0.5 mL solvent under nitrogen was added a solution of fluoride in ~0.2 to ~0.4 mL solvent. Upon completion of reaction, the solution was allowed to warm slowly to room temperature. An internal standard (n-nonane) was added (~5λ). The mixture was made to a standard volume (1 or 2 mL) by the addition of solvent, and was analyzed by GLC (Column A, 70°). Yields of 3,3,4,4,-tetramethyl-$\Delta^{1,2}$-diazetine are reported in Table IV.

Table IX. Yields of 3,3,4,4-Tetramethyl-$\Delta^{1,2}$-Diazetine from N,N'-Dichloro-2,2,4,4,5,5-hexamethyl-1,3-diaza-2-silacyclopentane.[a]

Fluoride	Equiv.	Conditions	Percent Yield Diazetine[b]	Characterization
n-$Bu_4N^+F^-$	2.1	THF, 0°, 4 hr	18	GLC
n$Bu_4N^+F^-$	2.0	Et_2O, 0°, 4 hr	14	GLC
$Et_4N^+F^-$	2.7	THF, 0°, 4 hr	24	GLC
n-$Bu_4N^+F^-$	2.1	THF, -78°, 5 hr	16	GLC
n-$Bu_4N^+F^-$	4.2	THF, 0°, 4 hr	42	GLC
n-$Bu_4N^+F^-$	2.1	THF, 0°, 2 hr	19[c]	GLC

[a]All reactions were conducted under a nitrogen atmosphere.

[b]Yields determined relative to nonane internal standared (GLC).

[c]Yield determined relative to a known concentration diazetine solution (GLC).

Table X . Reductions of 2,3-Dimethyl-2,3-dinitrobutane.

Method	Conditions	Product	Yield	Character-ization
Sn	Concd. HCl	Diamine	48%	Isolation; NMR
H_2, Pd/C	Acetic acid-Ethanol	Diamine diacetate salt	55%	Isolation; NMR
H_2, Pd/C	HCl-methanol	Diamine	43%	Isolation; NMR
H_2, Pd/C	Methanol	Diamine; acetone oxime	1:3	GLC
$NH_2NH \cdot H_2O$, PdC	Methanol	No Reaction	-	-
$LiAlH_4$	Ether or THF	No Reaction	-	-

Hydrogenation of 2,3-Dimethyl-2,3-dinitrobutane in HCl-Methanol. 2,3-Dimethyl-2,3-dinitrobutane (2.00 g, 11 mmol) was dissolved in 75 mL methanol and 1.5 mL concentrated HCl and was hydrogenated with 0.4 g 10% Pd/C with an initial pressure of 40 psi until hydrogen uptake ceased (84 hr). The mixture was acidified to pH 1.5 with concentrated HCl and was filtered through Celite. Solvents were removed by rotovap, and the residue was extracted with methylene chloride. The residue was added slowly to a few mL cold concentrated aqueous NaOH. The mixture was extracted continuously with ether for 48 hr. The ether was dried (K_2CO_3) and evaporated to afford 2,3-diamino-2,3-dimethylbutane (0.55 g, 43%) as an orange oil: NMR ($CDCl_3$) 1.12 (s, 12 H).

Hydrogenation of 2,3-Dimethyl-2,3-dinitrobutane in Acetic Acid-Ethanol. 2,3-Dimethyl-2,3-dinitrobutane (3.0 g, 17 mmol) was dissolved in 15 mL glacial acetic acid and 100 mL ethanol and was hydrogenated with 0.3 g 10% Pd/C with an initial pressure of 40.5 psi until hydrogen uptake ceased (24 hr). The mixture was filtered through Celite and evaporated under reduced pressure to afford a white solid. The solid was dissolved in a few mL ethanol with heating. The solution was triturated with ether to give 2,3-diamino-2,3-dimethylbutane diacetate salt (2.50 g, 62%) as a white solid: mp 152°; NMR (D_2O) 1.37 (s, 12 H), 1.83 (s, 6 H). The solid was dissolved in water, mixed with powdered K_2CO_3, and extracted with THF in a Sohxlet apparatus 5 hr to give the diamine as an oil: NMR ($CDCl_3$) 1.12 (s, 12 H), 1.5 (s, br, exch. D_2O).

Hydrogenation of 2,3-Dimethyl-2,3-dinitrobutane in Methanol.

2,3-Dimethyl-2,3-dinitrobutane (2.00 g, 11 mmol) was dissolved in 100 mL methanol and was hydrogenated with 0.7 g 10% Pd/C with an initial pressure of 42 psi until hydrogen uptake ceased (80 hr). The mixture was acidified to pH 2 with concentrated HCl, and was filtered through Celite. Evaporation under reduced pressure gave a yellow suspension. The suspension was extracted with methylene chloride. The aqueous portion was put into a few mL cold concentrated aqueous NaOH and was extracted continuously with ether 5 days. The ether was dried (K_2CO_3) and removed by distillation at atmospheric pressure. The resulting oil was analyzed by GLC (Column A, 105°) and was found to contain a 3:1 mixture of acetone oxime and 2,3-diamino-2,3-dimethylbutane.

4-Phenyl Urazole was made by the method of Cookson[58] by the alkaline hydrolysis of 1-ethoxycarbonyl-4-phenyl-semicarbazide[58] in 72% yield, as white needles: mp 205-207° (lit.[58] 209-210°).

4-Phenyl-1,2,4-triazoline-3,5-dione was made by the method of Wamhoff and Wald[59] by the N-bromosuccinimide oxidation of 4-phenyl urazole in 74% yield, as red needles: mp 165-170° (lit.[59] mp 166-172°). 4-Phenyl 1,2,4-triazoline-3,5-dione could be sublimed (.04 Torr, 93°) to give red needles: mp 170-175°.

4-Methyl-1,2,4-triazoline-3,5-dione was prepared by the method of Cookson[58] by the tert-butyl hypochlorite oxidation of 4-methyl-1,2,4-traizolidine-2,5-dione[58] in 85% yield, as bright pink needles: mp 102-104° (lit.[58] mp 104°). 4-Methyl-1,2,4-triazoline-3,5-dione could be sublimed (.07 Torr, 45-50°) to give needles: mp 103-104°.

Diels Alder-Diels Alder Adduct (2:1) of 4-Methyl-1,2,4-triazoline-3,5-dione and cis-Stilbene (15a). To a stirred solution of cis-stilbene (Aldrich, 316 mg, 1.75 mmol) in 2 mL methylene chloride (distilled from CaH_2) at 0° was added a solution of N-methyltriazolinedione (396 mg, 3.50 mmol) in 8 mL methylene chloride over 10 min in an apparatus shielded from light and under an argon atmosphere. After stirring for 30 min at 0°, the reaction mixture was allowed to warm to room temperature over 5 hr, after which time the reaction mixture was light yellow. The solvent was removed by rotary evaporation to give a quantitative yield of an off-white solid. Recrystallization from absolute methanol gave 15a as a white crystalline solid: mp 236-239° (dec.); ir ($CHCl_3$) 3010 (w), 1775 (s), 1720 (vs), 1460 (s), 1400 (s), 1360 (w), 1250 (m), 1020 (m), 910 (m), 885 (m), 700 (m); NMR ($CDCl_3$) (250 MHz), 3.03 (s, 3 H), 3.04 (s, 3 H), 4.19 (q, 1 H), 5.27 (d of d, 1 H), 5.40 (d of d, 1 H), 6.24 (d of d, 1 H), 6.35 (quint, 1 H), 6.62 (t, cplx, 2 H), 7.35 (m, cplx, 5 H); NMR ($DMSO-d_6$) (250 MHz), 2.87 (s, 3 H), 2.89 (s, 3 H), 4.45 (q, 1 H), 5.44 (d of d, 1 H), 5.48 (d of d, 1 H), 6.06 (quint, 1 H), 6.33 (d of d, 1 H), 6.65 (t, cplx, 2 H), 7.35 (m, cplx,, 5 H); ^{13}CNMR ($CDCl_3$) 157.28, 156.38, 153.43, 152.80 (carbonyl); 136.41, 129.90, 129.74, 129.08 (2C), 128.93, 127.48 (2C), 127.36, 126.76 (aryl and vinyl C); 58.45, 57.29, 53.59, 52.99, (C adjacent to N); 25.55, 24.95 ($N-CH_3$); mass spectrum 406 (M^+, 9.42), 293 (M^+-TAD, 71.3), 235 (30.4), 190 (37.4), 180 (43.9), 179 (56.1), 178 (56.1), 165 (57.5), 132 (100.0), 77 (50.6).

Anal. Calcd. for $C_{20}H_{18}N_6O_4$: C, 59.11; H, 4.46; N, 20.68. Found: C, 58.83; H, 4.54; N, 20.76.

Diels Alder-Diels Alder Adduct (2:1) of 4-Phenyl-1,2,4-triazoline-3,5-dione and cis-Stilbene (15b) was prepared by the procedure on the previous page. The crude product was recrystallized from absolute methanol to afford 15b as a white crystalline solid: mp 242-244° (dec.); ir ($CHCl_3$) 3020 (w), 1780 (s), 1720 (vs), 1600 (s), 1500 (s), 1410 (s), 1260 (m), 1145 (m); NMR ($CDCl_3$) 4.32 (s,br, 1 H), 5.40 (m, 2 H), 6.27 (m, 1 H), 6.57 (m, 1 H), 6.62 (t, 2 H), 7.28 (s, 5 H), 7.35 (s, 5 H); mass spectrum 530 (M^+, 0.35), 119 (52.2), 91 (59.5), 64 (32.14), 77 (38.9), 57 (100.0), 44 (69.2), 43 (80.7), 41 (68.0), 39 (35.7).

Anal. Calcd. for $C_{30}H_{22}N_6O_4$: C, 67.91; H, 4.18; N, 15.84. Found: C, 67.91; H, 4.45; N, 15.66.

Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione and trans-Stilbene. To a stirred solution of trans-stilbene (Aldrich, 258 mg, 1.43 mmol) in 5 mL dry methylene chloride at 0° was added a solution of N-methyltriazolinedione (332 mg, 2.94 mmol) in 25 mL methylene chloride over 45 min in an apparatus shielded from light and under argon. After stirring at 0° until the red color disappeared, the reaction mixture was allowed to warm to room temperature. The solvent was removed by rotary evaporation to give a mixture of two products. The resulting solid was stirred in 250 mL refluxing methanol and filtered. The filtrate was allowed to crystallize after concentration, and several crystal crops were taken. The first crop was enriched in the Diels Alder-Diels Alder adduct and was again recrystallized from methanol, giving as a first crop 17a as a flocculent white crystalline solid: mp 264-265°; ir ($CHCl_3$) 3020 (w), 1785 (s), 1720 (vs), 1460 (s), 1400 (s), 1365 (m), 1275 (m), 1030 (m), 1020 (m); NMR (DMSO-d_6) (250 MHz) 2.90 (s, 3 H), 2.93 (s, 3 H), 4.23 (q, 1 H), 5.49 (d of d, 1 H), 5.68 (t, 1 H), 5.97 (d of t, 1 H), 6.28 (t, 1 H), 6.74 (t, cplx, 2 H), 7.30 (m, cplx, 5 H); ^{13}C NMR (DMSO-d_6) 156.90 (2C) 155.69, 150.57 (carbonyl); 138.35, 129.61, 129.52, 128.67 (2C), 128.05, 126.78 (2C), 125.58, 125.40 (aryl and vinyl); 58.31, 54.63, 53.19, 53.10 (C adjacent to N); 25.08, 24.55 ($N-CH_3$)]. Mass spectrum 406 (M^+, 4.31), 203 (M^+ - TAD, 59.4), 190 (33.7), 180 (46.8), 179 (58.5), 178 (56.7), 165 (53.7), 132 (100.0), 89 (32.5), 77 (52.6).

Anal. Calcd. for $C_{20}H_{22}N_6O_4$: C, 59.11; H, 4.46; N, 20.68. Found: C, 58.94; H, 4.59; N, 20.72.

Subsequent crops precipitating were enriched in the Diels Alder-ene isomer (18a).

Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione and Styrene.

To a stirred solution of styrene (39 mg, 0.37 mmol) in 0.25 mL chloroform at room temperature was added a solution of N-methyltriazolinedione (88 mg, 0.78 mmol) in 0.75 mL chloroform dropwise. The solution decolorized instantly. The solution was stirred 30 min and the solvent was removed by rotary evaporation, resulting in a mixture of two compounds, Diels Alder-Diels Alder adduct (19a) and the Diels Alder-ene adduct (20a). The first crop precipitated upon recrystallization gave 20a as transparent plates: mp 278-279° (dec.); NMR (DMSO-d_6) (250 MHz) 2.91 (s, 3 H), 3.02 (s, 3 H), 3.93 (d of d, 1 H), 4.17 (d of d, 1 H), 5.52 (t, 1 H), 7.17 (m, 2 H), 7.45 (t of d, 1 H), 8.33 (d, J = 8.4, 1 H), 10.8 (s, br, 1 H); mass spectrum 330 (M^+, 1.85), 216 (M^+ - N-NH-, 50.87), 215 (M^+ - triazolidine, 22.1), 152 (15.2), 132 (100.0), 77 (21.7).

Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione and Styrene.[39]

To a stirred solution of styrene (106 mg, 1.02 mmol) in 5 mL dry methylene chloride at room temperature was added dropwise a solution of N-phenyltriazolinedione (356 mg, 2.03 mmol) in 20 mL methylene chloride. The red color was discharged instantly. The solution was stirred for 5 min and the solvent was removed by rotary evaporation to afford a solid. The solid was recrystallized from denatured alcohol. The first two crops precipitated contained mixtures of the Diels Alder-Diels Alder-ene products. The third crop precipitated afforded 20b as a white solid: mp 242° (dec.); ir (KBr) 3450 (br), 1770 (s), 1720 (vs), 1600 (m), 1495 (s), 1460 (m), 1420 (s), 1340 (m), 1140 (m), 1025 (m), 760 (s), 695 (s); NMR (DMSO-d_6) 4.23 (d, 1 H), 4.40 (d, 1 H), 5.73 (s, br, 1 H), 7.4-7.56 (m, 13 H), 8.40 (d, J = 8, 1 H), 10.3 (s, br, 1 H); mass spectrum 454 (M^+, 0.62), 278 (M^+ - N-NH-, 45.0), 277 (M^+ - triazolidine, 30.1), 159 (27.6), 132 (100.0), 130 (20.9), 119 (39.8), 103 (20.7), 77 (33.7).

Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione and 1,1-Diphenylethylene. To a stirred solution of 1,1-diphenylethylene (302 mg, 1.67 mmol) in 15 mL methylene chloride, protected from moisture, was added N-methyltriazolinedione (380 mg, 3.34 mmol) as a solid. After the solution had decolorized, the solvent was removed by rotary evaporation. The resulting solid was recrystallized twice from methanol, affording the Diels-Alder-Diels-Alder 21 as a flocculent white crystalline solid: mp 221-223°. IR (KBr) 1765 (s), 1700 (vs), 1600 (w), 1455 (s), 1390 (m), 1325 (m), 1280 (m), 1235 (w), 1180 (m), 1080 (m), 1015 (m), 755 (s), 725 (w), 700 (m); NMR ($CDCl_3$) 3.01 (s, 3 H), 3.14 (s, 3 H), 4.02 (d/d, 1 H), 4.22 and 4.62 (AB quartet, 2 H), 5.43 (d/d, 1 H), 6.31 (d/t, 1 H), 6.52 (t, cplx, 2 H), 7.52-7.59 (aryl, 5 H). In a run in acetone, the solvent was slowly evaporated as crystal crops were taken, giving a first crop with mp 252-260°. This solid was recrystallized twice from methanol to afford the Diels-Alder-ene adduct, 22 (79 mg, 8%) as a white crystalline solid: mp 260-261°; ir (KBr) 3400 (br), 1765 (s), 1700 (vs), 1600 (w), 1455 (s), 1390 (m), 1325 (m), 1280 (m), 1180 (m), 1080 (m), 1015 (m), 755 (s), 725 (w), 700 (m); NMR (DMSO-d_6) 2.88 (s, 3 H), 2.97 (s, 3 H), 4.40 and 5.12 (d, J = 12.8, AB quartet), 6.80-7.49 (m, 8 H), 8.20 (d, J = 8.5, 1 H).

Anal. Calcd. for $C_{20}H_{18}N_6O_4$: C, 59.11; H, 4.46; N, 20.68. Found: C, 58.56; H, 4.51; N, 20.32.

The compound was found to be insoluble in DMSO-d_6, CD_3CN, CD_3COCD_3, and $CDCl_3$.

2,3-Diphenyl-p-dioxene[60] was prepared by the reaction of benzoin with ethylene glycol in 30% yield; mp 88-92° (lit.[60] mp 95-96°); IR ($CHCl_3$) 3080 (w), 3060 (w), 2980 (m), 2930 (m), 2880 (m), 1640 (s), 1600 (m), 1490 (m), 1455 (m), 1445 (m), 1280 (s), 1255 (s), 1130 (s), 1100 (s), 1070 (s), 965 (s), 910 (s), 880 (s), 690 (s); NMR ($CDCl_3$) 4.20 (s, 4 H), 7.15 (s, 10 H).

Diels Alder-Diels Alder Adduct (2:1) of 4-Methyl-1,2,4-triazoline-3,5-dione and 2,3-Diphenyl-p-dioxene (23). To a stirred solution of 2,3-diphenyl-p-dioxene (380 mg, 1.78 mmol) in 20 mL methylene chloride at room temperature, protected from moisture, was added N-methyltriazoline-dione (400 mg, 3.53 mmol) as a solid. The solution was stirred at room temperature 18 hr, after which time the solution was pink. The solvent was evaporated to afford a pink solid. The solid was treated with acetone and cooled to -10°. Filtration gave 23 (177 mg, 23%) as a pale pink solid: mp 249-251°; ir (KBr) 2960 (w), 1770 (s), 1705 (vs), 1460 (s), 1390 (s), 1270 (m), 1175 (m), 1080 (m), 1025 (m), 960 (m), 915 (m), 880 (m), 745 (s); ir ($CHCl_3$) 1770 (m), 1720 (s), 1500 (m), 1450 (w), 1400 (s), 1200 (w), 710 (s); NMR (DMSO-d_6) (250 MHz) 2.85 (s, 3 H), 2.91 (s, 3 H), 4.3 (cplx m, 4 H), 4.51 (s, 1 H), 5.61 (s, 1 H), 6.08 (s, 2 H), 7.2 (aryl, 5 H).

A small portion of the isolated product was insoluble in DMSO-d_6 and had mp 255-256° (to a brown melt).

Diels Alder-Diels Alder Adduct (2:1) of 4-Phenyl-1,2,4-triazoline-2,5-dione and 2,3-Diphenyl-p-Dioxene (24). 2,3-Diphenyl (200 mg, 0.93 mmol) and N-phenyltriazolinedione (327 mg, 1.86 mmol) were dissolved in 5 mL benzene to give a red solution. The mixture was heated to reflux under argon, protected from light. After six hours, the solution was pale yellow. Evaporation of solvent afforded an off-white solid. The solid was treated with 5 mL acetone and cooled to -10°. Filtration gave (24) (390 mg, 74%)as a white crystalline solid: mp 248-250° (to a brown foam); ir (KBr) 1780 (s), 1720 (vs), 1490 (s), 1450 (w), 1405 (s), 1280 (m), 1215 (m), 1180 (m), 1120 (m), 1075 (m), 750 (s); NMR (DMSO-d_6) 4.20 (m, 4 H), 4.75 (d, 1 H), 5.79 (d/d, 1 H), 6.25 (d, 1 H), 6.84 (t, 2 H), 7.0-8.0 (aryl, 15 H).

Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione with trans-1-Phenylpropene. To a solution of trans-1-phenylpropene (256 mg, 2.17 mmol) in 25 mL methylene chloride at room temperature was added N-methyltriazolinedione (493 mg, 4.36 mmol). The solution decolorized immediately and solvent was removed by rotary evaporation. Recrystallization from 250 mL methanol (reduced to 150 mL by boiling) gave the Diels Alder-Diels Alder adduct (2:1) 25 (133 mg, 26%) as fine white needles: mp 257-258° (to a red melt); ir (KBr) 2980 (m), 1760 (vs), 1450 (s), 1385 (s), 1355 (m), 1305 (w), 1270 (w), 1260 (w), 1240 (m), 1210 (m), 1175 (s), 1150 (m), 1100 (w), 1085 (m), 1040 (m), 1020 (s), 960 (w), 940 (w), 900 (m), 870 (s), 800 (m), 775 (s), 750 (s), 740 (m), 730 (s), 715 (m), 705 (w); NMR (DMSO-d_6) 1.13 (d, 3 H, J = 7), 2.86 (s, 3 H), 2.93 (s, 3 H), 4.07 (q, 1 H), 4.60 (d/t, 1 H), 5.42 (d/d, 1 H), 5.90 (d/t, 1 H), 5.21 (t, 1 H), 6.68 (t, cplx, 2 H).

Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C, 52.32; H, 4.68; N, 24.41. Found: C, 51.84; H, 4.89; N, 24.24.

Further recrystallization from methanol gave the Diels Alder-ene adduct (2:1) 26 (278 mg, 55%) as transparent plates: mp 228-233° (to a clear melt); ir (KBr) 3420 (m), 2980 (m), 1750 (s), 1690 (vs), 1600 (m), 1580 (m), 1450 (s), 1385 (s), 1370 (m), 1300 (m), 1270 (m), 1200 (m), 1160 (m), 1075 (m), 1010 (s), 970 (m), 895 (s), 870 (m), 760 (s), 740 (s), 700 (s), 650 (s); NMR (DMSO-d_6) 1.12 (d, J = 6), 2.90 (s, 3 H), 3.04 (s, 3 H), 4.65 (q/d, 1 H), 5.32 (d, J = 1.9, 1 H), 7.14-7.52 (3 H, aryl), 8.28 (d, J = 8.6, 1 H).

No evidence for ene product of triazolinedione and trans-1-phenyl propene was found upon examination of the crude mixture by NMR.

Product Distributions from Reactions of Triazolinedione with Phenyl Substituted Ethylenes. To a solution of the olefin (ca. 0.1 M) was added two equivalents of triazolinedione at room temperature with stirring. The solvent was removed by rotary evaporation and the residue was completely dissolved in DMSO-d_6. The 250 MHz NMR spectrum of the crude products was observed, and percentages of products were calculated from integration.

Relative Rates of Reactions of Phenylethylenes Toward 4-Methyl-1,2,4-triazoline-3,5-dione. Equimolar amounts (60-120 mg) of two olefins were dissolved in methylene chloride (concentration, ~0.1 M) and cooled to 0°. 4-Methyl triazoline-dione was added as a solid (total olefin concentration/TAD concentration ≃ 1.0). After reaction was complete, solvents were evaporated. The crude mixture was completely dissolved in DMSO-d_6, and was analyzed by 250 MHz NMR.

Table XI. Yields of the [2+2] Adduct of N-Phenyltriazolinedione and Indene.[a]

Solvent	Temperature	Other	Yield
CH_2Cl_2	-70°	-	69%, isolated
CH_3CN	-45°	-	58%, isolated
CH_3CN	20°	-	42%, isolated
CH_2Cl_2	20°	-	40% (NMR)
CH_2Cl_2	20°	20 mole % Sumilizer WXR [b] added	47% (NMR)

[a] Reactions were run using a 1:1 mole ratio of indene to N-phenyl triazolinedione.

[b] 4,4'-thiobis (6-tert-butyl)-3-methylphenol.

1,1,2,2a,7b-Tetrahydro-3H-indene [2,1,c] 1,2-diazete-1,2-dicarboxylic acid N-Phenylimide[25] (27). Indene (redistilled, 253 mg, 2.18 mmol) was dissolved in 80 mL methylene chloride and cooled to -70°. N-Phenyltriazolinedione (381 mg, 2.18 mmol) was added in one portion with stirring as a solid, forming a suspension. This suspension was stirred 30 min at -70° and was allowed to warm to -10° over 3 hr. The solution was warmed to room temperature, after which time the solution was pale pink-orange. Evaporation of solvent gave a quantitative yield of a pale orange solid, mp 145-165° (dec.). The solid was put in 6 mL dry benzene, forming a thick yellow slurry. The mixture was stirred 15 min; the solid was filtered and the filter cake was washed with 3 mL more dry benzene. Drying under high vacuum (1 Torr) gave the diazetidine (436 mg, 69%), mp 167-168°. Recrystallization from chloroform-ether gave a white solid: mp 173-175° (lit.[25] mp 166-167.5°); ir ($CHCl_3$) 3000 (w), 1770 (m), 1715(vs), 1600 (w), 1500 (s), 1455 (w), 1390 (s), 1305 (m), 1120 (s), 1005 (s); (KBr) 1770 (m), 1715 (vs), 1490 (s), 1390 (s); NMR ($CDCl_3$) 3.16 (d/d, 1 H), 3.78 (d, 1 H), 5.30 (t, 1 H), 5.84 (d, 1 H), 7.0-7.4 (m, 4 H), ^{13}C NMR ($CDCl_3$) 161.10 (carbonyl),160.78 (carbonyl), 142.56, 134.52, 131.14, 130.75, 129.16, 128.60, 128.02, 127.22, 125.84, 125.51, 73.56 (C adjacent to N, benzylic), 67.14 (C adjacent to N), 34.55 (benzylic C); mass spectrum 291 (M^+, 0.41), 116 (100), 115 (38.45), 117 (12.53), 119 (11.92), 91 (11.71).

Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione with Indene in Acetonitrile at Low Temperature. To a solution of indene (256 mg, 2.2 mmol) in 80 mL acetonitrile (spectrograde, distilled from CaH_2 under argon), protected from light and moisture and cooled to -45°, was added N-phenyltriazolinedione (381 mg, 2.2 mmol) as a solid. The solution was kept cold 15 min, and was allowed to warm to room temperature over 1 hr. The solution was evaporated by rotovap and high vacuum to give a gummy solid. The solid was treated with 10 mL dry benzene to give a yellow slurry. The slurry was filtered, washing the filter cake with 1 mL benzene, giving diazetidine 27 (365 mg, 58%) as a white solid: mp 169-171° (lit.[25] mp 166-167.5). Partial evaporation of the filtrate gave more of the diazetidine, isolated by filtration (40 mg, 6%): mp 162-165°.

Reaction of Indene with Triazolinedione in the Presence of a Phenol.

To a solution of indene (57 mg, 0.5 mmol) in 10 mL methylene chloride at room temperature was added N-phenyltriazolinedione (86 mg, 0.5 mmol). After the solution decolorized, solvent was removed under reduced pressure. The crude product was found to contain 40% diazetidine by NMR.

To a solution of indene (59 mg, 0.5 mmol) in 10 mL methylene chloride at room temperature was added 4,4'-thiobis (6-tert-butyl)-3-methyl phenol (35 mg, 0.1 mmol) and N-phenyltriazolinedione (89 mg, 0.5 mmol). After the solution decolorized, solvent was removed by rotary evaporation. The crude product was found to contain 47% diazetidine by NMR, essentially the same result as in the absence of the phenol.

Polymeric Product from Reaction of Triazolinedione with Indene (28). To a solution of indene (redistilled, 403 mg, 3.47 mmol) in 100 mL methylene chloride at room temperature was added N-phenyltriazolinedione (608 mg, 3.47 mmol). The solution became yellow. Additional N-phenyltriazolinedione (75 mg, 0.43 mmol) was added. The solution remained slightly pink after stirring several minutes, and was decolorized by the addition of one drop indene. Evaporation of solvent afforded a tan solid. The solid was dissolved in 10 mL benzene. The solution was cooled to 5° as a fine precipitate formed. The solid was removed by filtration and was washed with a few mL benzene, affording a white solid, the diazetidine (320 mg, 32%): mp 166-168° (lit. mp 166-167.5°). The brown filtrate was evaporated to afford a brown gummy solid. The solid was dissolved in dry benzene and was concentrated to a volume of 10 mL by boiling. The solution was triturated with ether. The precipitate was filtered and washed with a little ether, giving a tan solid (460 mg, 45%) melting from 180-184°. The NMR spectrum of this solid showed the diazetidine and broad peaks at 3 to 4 ppm, 7 to 8 ppm, and a small singlet at 2.45 ppm.

The tan solid was dissolved in 10 mL hot THF, forming a chestnut brown solution. The solution was cooled and 15 mL ether was added. Cooling gave a precipitate; the solid was isolated by filtration at intervals. The first crop precipitated (mp 182°) was dissolved in hot THF and was triturated with ether to afford a tan solid that formed a red-brown chloroform solution: ir ($CHCl_3$) 3000 (w), 1770 (m), 1715 (vs), 1605 (s), 1495 (s), 1460 (m), 1440 (m), 1415 (m), 1300 (m), 1200 (w); NMR ($CDCl_3$) 7.2 (br), 5.0 (br), and 3.2 (br) (area 17 : 1 : 2); ^{13}C NMR

129, 125, 128, 131 (broad peaks).

Anal. Calcd. for $C_{17}H_{13}N_3O_2$: C, 70.09; H, 4.50; N, 14.43. Found: C, 67.88; H, 4.69; N, 14.37.

2,3-Dimethyl Fumaric Acid was synthesized by a modification of literature methods.[61] Dimethyl maleic anhydride (Aldrich, 35.2 g, 279 mmol) was dissolved in a solution of 195 g NaOH in 455 mL water. The mixture was refluxed 20 hr and was allowed to cool. With cooling, the mixture was acidified to pH 13 with 360 mL conc. HCl. The mixture was further acidified by the portionwise addition of a total of 47 mL more conc. HCl. The precipitates formed were filtered at pH 5, pH 4, pH 3.5, pH 3, pH 2.5, and pH 2. The solid precipitating between pH 3 and pH 5 consisted of a mixture of dimethyl maleic anhydride and a small amount of 2,3-dimethyl fumaric acid. The bulk of the dimethyl fumaric acid precipitated below pH 3 and had mp 235-239°. The solid was washed with methylene chloride to give 2,3-dimethyl fumaric acid (9.2 g, 23%), which was purified by recrystallization from hot water to afford white needles: mp 236-238° (lit.[61b] mp 245°).

2,3-Dimethyl fumaric acid could also be prepared by bomb reaction at 185° for 45 hr, but the product obtained was yellow.

Dimethyl 2,3-dimethyl Fumarate was synthesized by the method of Shimamura.[62] 2,3-Dimethyl fumaric acid (9.2 g, 64 mmol) was refluxed for 46 hr in a mixture of 13 mL conc. H_2SO_4 and 125 mL absolute methanol. The mixture was allowed to cool, was flooded with ca. 200 mL water and was extracted with ether. The ether extracts were washed successively with water, saturated aqueous sodium bicarbonate solution, again with water, and were dried ($MgSO_4$). Evaporation of solvent afforded dimethyl 2,3-dimethyl fumarate (9.40 g, 85%) as a clear oil: NMR ($CDCl_3$) 2.08 (s, 6 H), 3.77 (s, 6 H).

Trans-1,1,4,4-tetradeuterio-2,3-dimethyl-2-butene-1,4-diol was made by the method of Kuhn et al.[63] To a solution of lithium aluminum deuteride (1.80 g, 43.7 mmol) in 100 mL diethyl ether (distilled from $LiAlH_4$) under an argon atmosphere with stirring was added a solution of dimethyl 2,3-dimethyl fumarate (5.90 g, 34 mmol) in 10 mL diethyl ether dropwise at a rate so as to maintain a gentle reflux. The solution was refluxed one hour more and was stirred at room temperature 2 hr. The mixture was quenched by the cautious addition of ether wet with D_2O and then with D_2O. The mixture was filtered. The white precipitate was washed by stirring with ether and was filtered. The combined filtrates were dried ($MgSO_4$) and the ether was removed by rotary evaporation to afford trans-1,1,4,4-tetradeuterio-2,3-dimethyl-2-butene-1,4-diol (2.05 g, 50%) as a clear oil that solidified on cooling: NMR ($CDCl_3$) 1.83 (s, 6 H). The NMR spectrum of the product also contained small signals at 1.2 ppm which could not be identified.

The oil was used without further purification.

Trans-1,4-dichloro-1,1,4,4-tetradeuterio-2,3-dimethyl-2-butene was made by literature methods.[64,65] To a suspension of N-chlorosuccinimide (8.01 g, 60 mmol) in 180 mL dry methylene chloride under nitrogen at 0° with stirring was added a solution of dimethyl sulfide (5.4 mL, 73 mmol) in 15 mL methylene chloride over a few minutes. The solution became milky and was cooled with stirring to -40°. Trans-1,1,4,4-tetradeuterio-2,3-dimethyl-2-butene-1,4-diol (3.61 g, 30 mmol) was dried in 100 mL methylene chloride with $MgSO_4$. The resulting solution was added dropwise over 15 min. The mixture was stirred at -40° 20 min. The clear solution was warmed to -20° over 1 hr. The solution was warmed to 0° over 45 min more and was stirred at 0-10° 1.5 hr. The clear solution was poured into 100 mL cold saturated NaCl in a separatory funnel and was shaken. Layers were separated. The aqueous portion was extracted twice with 50 mL portions of ether. The ether washings were combined with the methylene chloride layer, and this was washed twice with 100 mL portions of cold saturated NaCl. The solution was dried ($MgSO_4$) and solvents were removed to afford the dichloride (4.28 g, 90%) as a pale yellow oil which darkened on standing: ir ($CHCl_3$) 2960 (s), 2930 (s), 2880 (m), 2180 (w), 2140 (w), 1770(vs), 1720 (s), 1450 (s), 1380 (s), 1270 (s), 1030 (s), 980 (s), 965 (m), 905 (m); NMR ($CDCl_3$) 1.90 (s, 6 H) and impurities at 2.3 and 4.7 ppm.

The crude dichloride was used without further purification.

Trans-1,1,1,4,4,4-hexadeuterio-2,3-dimethyl-2-butene was prepared by the method of Stephenson.[65] To a slurry of lithium aluminum deuteride (4.48 g, 109 mmol) in 65 mL dry diglyme (refluxed at least 96 hr over sodium and freshly distilled) at -60° under nitrogen with stirring was added a solution of cis-1,4-dichloro-1,1,4,4-tetradeuterio-2,3-dimethyl-2-butene (4.28 g, 27.2 mmol) in 7 mL dry diglyme by syringe over 15 min. The mixture was stirred below -50° 15 min and was allowed to warm to room temperature gradually 4.5 hr. The product was carefully distilled from the crude reaction mixture into a dry ice cooled receiver in ca. 35% yield: NMR ($CDCl_3$) 1.67 (s, 6 H) and signals for traces of diglyme and dimethyl sulfide.

The oil was used without further purification.

Dimethyl-2,3-dimethyl Maleate was prepared by a modification of literature methods.[66] 2,3-Dimethyl maleic anhydride (9.9 g, 78.5 mmol) and sodium carbonate (8.50 g, 80 mmol) were dissolved in 100 mL water. The solution was refluxed 1.5 hr and cooled. Water was removed by rotary evaporation to afford a mushy solid. The solid was put in 600 mL 95% ethanol, giving a thick slurry which was stirred 15 min. The slurry was filtered and the solvent was removed from the filtrate by vacuum. The resulting solid was treated with enough 95% ethanol to form a slurry. This mixture was stirred 15 min and was then filtered. The combined precipitates were oven dried at 100°, affording a quantitative yield of disodium 2,3-dimethyl maleate as a white solid not melting below 300°: NMR (D_2O) 1.76 (s).

Disodium 2,3-dimethyl maleate was dissolved in 500 mL water. A solution of silver nitrate (27.0 g, 159 mmol) in 100 mL water was added dropwise and the mixture was stirred 1 hr. The solution was filtered and the precipitate was washed with methanol and then ether. The resulting finely divided, light-sensitive solid, disilver 2,3-dimethyl maleate was oven dried 30 min at 100°.

Disilver 2,3-dimethyl maleate was suspended in 250 mL diethyl ether (Mallinckrodt, freshly opened cans) and was treated with methyl iodide (120 mL, 370 mmol) under nitrogen and shielded from light. The suspension was stirred at reflux for 48 hr. The mixture was filtered, the filtrate dried ($MgSO_4$) and the solvent removed by vacuum to afford dimethyl 2,3-dimethyl maleate (7.49 g, 55% based on starting anhydride) as a clear oil: ir ($CHCl_3$) 3000 (m), 2960 (s), 1720 (s), 1640 (m), 1435 (s), 1380 (m), 1290 (s), 1170 (m), 1040 (m), 930 (m), 840 m); NMR ($CDCl_3$) 1.91 (s, 6 H), 3.72 (s, 6 H).

Cis-1,1,4,4-tetradeuterio-2,3-dimethyl-2-butene-1,4-diol was made by the method described above for the trans-isomer.[63] The deuterated diol was obtained in 85% yield: ir ($CHCl_3$) 3400 (br), 2960 (m), 2930 (m), 1450 (m), 1380 (w), 1260 s), 1220 (s), 1100-1000 (s, br), 950 (m); NMR ($CDCl_3$) 1.77 (s, 6 H).

The oil was used without further purification.

Cis-1,4-dichloro-1,1,4,4-tetradeuterio-2,3-dimethyl-2-butene was prepared by the method described for the trans isomer:[64,65] ir ($CHCl_3$) 2960 (s), 2930 (s), 2180 (m), 1450 (m), 1385 (m), 1325 (w), 1285 (w), 1260 (s), 1080 (br), 1020 (br), 965 (s), 910 (m), 870 (m); NMR ($CDCl_3$) 1.83 (s) and traces of methyl sulfide and diester.

The dichloride was used without further purification.

Cis-1,1,1,4,4,4-hexadeuterio-2,3-dimethyl-2-butene was prepared by the method described for the trans isomer.[65] The product was carefully distilled from the crude reaction mixture through a bulb to bulb apparatus into a dry ice cooled receiver in ca. 40% yield: NMR ($CDCl_3$) 1.63 (s, 6 H). The product contained traces of diglyme and dimethyl sulfide, and was used without further purification.

1,1,1-Trideuterio-2-trideuteriomethyl-3-methyl-2-butene was prepared by heating solutions of 3,3-dimethyl-4,4-trideuteriomethyl-β-lactone[67] in $CDCl_3$ in sealed tubes at 110°.

Kinetic Isotope Effect Studies with Triazolinediones by NMR.

To a solution of deuterioolefin in $CDCl_3$ (ca. 0.2 M) in an NMR tube at room temperature was added 4-methyl-1,2,4-triazoline-3,5-dione (sublimed) or 4-phenyl-1,2,4-triazoline-3,5-dione (sublimed) until a pale pink color persisted. The solutions were analyzed by 250 MHz NMR, and kinetic isotope effects were calculated from the integrations.

Adamantylideneadamantane was prepared according to the method of McMurry.[46] Standard anaerobic glove bag, Gooch tube, and cannulation techniques were used for the transfer of air and water sensitive reagents. All glassware was oven dried (at 120° > 12 hr) and cooled under a stream of argon. Dimethoxyethane was predried over NaOH and was fractionally distilled from powdered CaH_2. The fractions boiling from 84-85° were collected. These fractions were refluxed under argon over a small amount of purified sodium for one hour, after which time the sodium was a yellow-gold color. The still was treated with a small amount of benzophenone and was run with magnetic stirring. Within two hours, a blue color in the liquid was apparent. A small amount of sodium was added; reflux was continued, and in a few hours, the still became purple. The dry, deoxygenated DME was collected under argon in dry glassware and was stored over activated Linde molecular sieves.

A 2L 3-necked round bottomed flask fit with a reflux condenser, overhead stirrer, argon flow, and Gooch tube was charged with titanium trichloride (Alfa, 59.3 g, 384 mmol). About 600 mL dry DME was added to the flask under argon (caution: the mixture becomes very warm). The DME and $TiCl_3$ were mixed with the stirrer occasionally to form a purple slurry. Lithium wire (Licoa Co., 8.00 g, 1.152 mol) was washed with petroleum ether and weighed. (Lengths of 2-3" were cut.) The wire was etched to brilliance in anhydrous methanol (Mallinckrodt), rinsed quickly in petroleum ether (Mallinckrodt, distilled from $KMnO_4$), and was cut into small pieces (0.5 cm long) directly into the reaction mixture under an argon flow. The flask was stoppered, and the mixture was refluxed 1 hr, forming a black slurry. The mixture was cooled

slightly, and adamantanone (Aldrich, 14.42 g, 96 mmol) was added to the flask in one portion. The mixture was refluxed under argon 21 hr. The mixture was cooled, with stirring, to room temperature. At 5 min intervals was added petroleum ether (6 x 100 mL). The ether was removed by decanting, and the black slurry remaining was washed with petroleum ether (8 x 50 mL) using overhead stirring. The ether washings were filtered through Florisil (45 g) in a 60 mL sintered glass funnel. The filter pad was washed with petroleum ether (400 mL). The ether washings were combined and evaporated to afford 11.3 g (88%) of a white solid: mp 155-175°. Recrystallization from methanol (3L) gave 9.8 g (76%) colorless needles of adamantylideneadamantane: mp 184-186° (lit.[46b] mp 183-184°); ir ($CHCl_3$) 2950 (s), 2900 (s), 2840 (s), 1460 (m), 1445 (s), 1440 (s), 1350 (m), 1330 (m), 1305 (w), 1295 (w), 1090 (s), 1060 (m), 1035 (w), 985 (w), 965 (m), 955 (m), 930 (m); ^{13}C NMR ($CDCl_3$) 133.38 (2C, olefinic), 39.74 (8C, methylene), 37.47 (2C, methylene), 32.02 (4C, methine), 28.67 (4C, methine); mass spectrum 268 (M^+, 100.0).

Adamantylideneadamantane was also made from adamantanone with $TiCl_3$ and Zn/Cu.[46a] Standard anaerobic glove bag, Gooch tube, and cannulation techniques were used for the transfer of air and water sensitive reagents. All glassware was flame-dried and cooled under a stream of argon. Water was deoxygenated by boiling with an argon purge and cooling with an argon purge. Zinc (19.6 g, activated)[68] was put into 80 mL deoxygenated water under argon. $CuSO_4$ (1.5 g) was added. The mixture was stirred 10 min while argon was bubbled through it, forming a black suspension. The solid was filtered under argon; the filter cake was washed with deoxygenated water, acetone, and ether. The solid was then dried under high vacuum 1.5 hr, affording the zinc-copper couple.

A dry 1 L 3-necked round bottomed flask was fit with a condenser, Gooch tube, and overhead stirrer. Titanium trichloride (Ventron, 33.0 g, 214 mmol) was anaerobically transferred to the flask, followed by 400 mL DME. Zinc-copper couple (31.0 g, 377 mmol) was added to the mixture. The Gooch tube was replaced with a glass stopper, and the mixture was heated to reflux with stirring under argon 45 min. A blue-green suspension resulted. Adamantanone (Aldrich, 5.9 g, 39 mmol) was dissolved in 50 mL dry DME and was added to the reaction mixture over 5 min. The mixture was refluxed 14 hr and was cooled to room temperature. The slurry was filtered through a 1 cm. pad of Florisil under an argon flow; the filter cake was thoroughly washed with petroleum ether (300 mL). The filtrate was evaporated to give 12.6 g black gummy solid. The solid was stirred with 400 mL petroleum ether with warming for 30 min, giving a pale orange solution. The solution was filtered. The filtrate

was dried over $MgSO_4$ and was evaporated under reduced pressure to afford 9.5 g pale orange solid. The solid was stirred with 400 mL warm hexane, and the liquid was filtered while warm. The filtrate was dried ($MgSO_4$) and was evaporated under reduced pressure to afford 4.15 g yellow solid which was found (GLC) to contain 87% adamanylideneadamantane. The overall yield of olefin was 69%. The product could be further purified by column chromatography on silica with hexane, or by recyrstallization from diethyl ether and then from hexane.

[2+2] Adduct of 4-Methyl-1,2,4-triazoline-3,5-dione and Adamantylideneadamantane. 4-Methyl-1,2,4-triazoline-3,5-dione and adamantylideneadamantane (1:1) were allowed to react in a variety of solvents ($CHCl_3$, CH_2Cl_2, CCl_4, benzene, acetone, ether, and CH_3CN), affording a quantitative yield of the [2+2] adduct. Recrystallization from ether gave white needles: mp 220-221° (to a red melt); ir ($CHCl_3$) 2910 (s), 2860 (s), 1730 (s), 1675 (vs), 1470 (m), 1455 (m), 1435 (s), 1385 (s), 1320 (w), 1095 (m), 1030 (w), 980 (m), 975 (m), 950 (w), 890 (m), 875 (w); NMR ($CDCl_3$) (250 MHz) 1.79 (m, 12 H), 1.98 (s, br, 4 H), 2.12 (d, 4 H), 2.43 (s, 4 H), 2.66 (d, 4 H), 3.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) 154.43 (2C, carbonyl), 90.64 (2C, quaternary), 38.21 (2C, methylene), 35.44 (4C, methylene), 34.59 (4C, methylene), 32.47 (4C, methine), 26.94 (2C, methine), 26.73 (2C, methine), 26.17 ($N-CH_3$); mass spectrum 268 (60.11).

Anal. Calcd. for $C_{23}H_{31}N_3O_2$: C, 72.41; H, 8.19; N, 11.01. Found: C, 72.47; H, 8.60; N, 10.99.

[2+2] Adduct of 4-Phenyl-1,2,4-triazoline-3,5-dione and Adamantylideneadamantane. 4-Phenyl-1,2,4-triazoline-3,5-dione and adamantylideneadamantane (1:1) were allowed to react in several solvents, affording a quantitative yield of the [2+2] adduct. The product was dissolved in refluxing dry THF and was triturated with pentane to afford flocculent white crystals: mp 229-231°; ir ($CHCl_3$) 2910 (s), 2860 (M), 1740 (s), 1680 (vs), 1500 (m), 1420 (m), 1405 (m), 1385 (s), 1375 (s), 1360 (m), 1160 (m), 1095 (w), 865 (m); ir (KBr) 2880 (s), 1740 (s), 1675 (vs), 1490 (s), 1470 (s), 1455 (s), 1360 (s), 1320 (m), 1170 (m), 1120 (m), 1095 (m), 1060 (w), 1010 (w), 980 (w), 870 (m), 820 (m), 755 (s), 715 (s); NMR ($CDCl_3$) 1.90 (br, 18 H), 2.60 (br, 8 H), 2.85 (br, 2 H), 7.40 (br, cplx, 5 H); ^{13}C NMR ($CDCl_3$) 153.19 (2C, carbonyl), 91.75 (2C, quaternary), 38.23 (2C, methylene), 35.56 (4C, methylene), 34.67 (4C, methylene), 32.55 (4C, methine), 26.99 (2C, methine), 26.78 (2C, methine); UV (CH_2Cl_2) $\lambda_{max} < 220$ nm ($\varepsilon > 10,000$), shoulder at 275 nm ($\varepsilon \sim 200$); mass spectrum 268 (45.78), 119 (60.84).

Anal. Calcd. for $C_{28}H_{33}N_3O_2$: C, 75.81; H, 7.50; N, 9.47. Found: C, 75.41; H, 7.62; N, 9.52.

(1,1-Dimethyl-2-methyl-2-propenyl)-4-methyl-1,2,4-triazolidine-3,5-dione. A solution of 2,3-dimethyl-2-butene (Aldrich 98%) in methylene chloride was stirred at room temperature while a solution of N-phenyltriazolinedione in methylene chloride was added until a faint pink color persisted. The solvent was removed by rotovap to give a nearly quantitative yield of an off-white solid. The solid was dissolved in refluxing dry THF and was triturated with pentane to give flocculent off-white crystals: mp 127-128°; ir ($CHCl_3$) 3360 (m), 3150 (m, br), 3060 (m, br), 2980 (m), 1760 (s), 1695 (vs), 1595 (m), 1500 (s), 1420 (s), 1375 (w), 1160 (m), 1120 (m), 1070 (w), 1010 (w), 905 (s), 855 (s); NMR ($CDCl_3$) 1.60 (s, 6 H), 1.85 (s, 3 H), 4.98 (s, 2 H), 7.38 (s, 5 H), 7.90 (s, br, 1 H); UV (CH_2Cl_2) λ_{max} < 220 nm (ε > 5000); mass spectrum 259 (0.49), 177 (4.50), 119 (5.79), 83 (96.23).

Anal. Calcd. for $C_{14}H_{17}N_3O_2$: C, 64.85; H, 6.61; N, 16.20. Found: C, 64.35; H, 6.67; N, 15.99.

Reversal of [2+2] Adduct Formation. The [2+2] adduct of N-phenyltriazolinedione and adamantylideneadamantane was dissolved in deuteriochloroform with an excess of 2,3-dimethyl-2-butene. The mixture was heated at reflux 3 days, protected from moisture and shielded from light. The solvent was evaporated, and the mixture was analyzed by NMR, which showed adamantylideneadamantane and the ene adduct of TAD and tetramethylethylene. The mixture was chromatographed on silica (CH_2Cl_2), affording the ene adduct of TAD and tetramethylethylene (IR, mass spectrum identical to an authentic sample) and adamantylidene-adamantane (IR, mass spectrum identical to an authentic sample).

Reversal of Indene Diazetidine Formation. 1,1,2,2a,7b-Tetrahydro-3H-indeno [2,1,c]-1,2-diazete-1,2-dicarboxylic acid N-phenylimide (104 mg, 0.35 mmol), mp 170-171°, was heated in $CDCl_3$ with 2,3-dimethyl-2-butene (400 µL, 3.8 mmol) at 65° for 7 days with stirring and protected from moisture. The solution was evaporated and dried under high vacuum to afford 111 mg of a semisolid. The residue was dissolved in $CDCl_3$, and a small amount of undissolved solid was removed by filtration.

The NMR spectrum of the mixture showed about equal amounts of starting diazetidine and ene adduct of TAD and 2,3-dimethyl-2-butene, with a trace of indene. Little if any polymeric product was apparent in the NMR spectrum.

7,7-Dimethoxybicyclo [2.2.1.] hept-2-ene was prepared according to the method of Gassman and Pape.[50] Sodium (125.0 g, 5.43 g-atoms) was out into very small pieces (<1 cm) and added to 1.5 L dry tetrahydrofuran in a 3 mL 3-necked round bottomed flask fit with an overhead stirrer with a Teflon paddle, condenser, dropping funnel, heating mantle, and argon flow. Tert-butanol (190 mL, 2.0 mol, distilled from CaH_2) was added to the mixture with stirring. The mixture was stirred 30 min at room temperature and was warmed to a gentle reflux. A solution of 7,7-dimethyoxy-1,2,3,4-tetrachlorobicyclo [2.2.1.] hept-2-ene (106 g, 0.363 mol) in 100 mL THF was added dropwise to the heated mixture over 2 hr. The mixture was heated at reflux under argon with stirring 19 hr more, after which time the sodium had fused into a large ball and the mixture was dark grey. After cooling, the liquid was decanted and mixed gradually with 600 mL methanol. The solution was poured over 2 L chopped ice and 500 mL ether with stirring. A dark, thick bottom layer was separated. The remaining mixture was extracted 4 times with 1 L portions water and then twice with 500 mL portions saturated aqueous NaCl. The mixture was dried ($MgSO_4$) and evaporated to give a brown oil. Distillation gave 7,7-dimethoxybicyclo [2.2.1] hept-2-ene (24.80 g, 44%) as a pale yellow oil: bp 92-98°, 35-40 Torr (lit.[50] bp 58-68°, 17 Torr); ir ($CHCl_3$) 2980 (s), 2940 (s), 2730 (m), 1500 (m), 1405 (s), 1385 (m), 1170 (s), 1130 (s), 1100 (s), 1060 (s), 1015 (s), 960 (s), 700 (m, br), 660 (m); NMR ($CDCl_3$) 0.8-2.1 (m, cplx, 4 H), 2.8 (m, cplx, 2 H), 3.15 (s, 3 H), 3.20 (s, 3 H), 6.06 (t, J=2, 2 H).

Reaction of Bicyclo [2.2.1] hept-2-en-7-one and N-Phenyltriazolinedione.

Bicyclo [2.2.]] hept-2-en-7-one[50a] and N-phenyltriazolinedione were heated in refluxing benzene or deuteriochloroform (ca. 1 M.) under argon. The solution was decolorized after 24 hr, and had precipitated a pale orange solid. The precipitate and solution were analyzed by NMR, and were found to contain products of decomposition of triazolinedione[69] and starting ketone only.

Reaction of Bicyclo [2.2.1] hept-2-en-7-one, Norbornene, and N-Phenyl triazolinedione. Bicyclo [2.2.1] hept-2-en-7-one (35 mg, 0.3 mmol), norbornene (30 mg, 0.3 mmol) and N-phenyltriazolinedione (56 mg, 0.3 mmol) were stirred in 1 mL deuteriochloroform at room temperature. After 8 hr, the reaction mixture was examined by NMR. Products of reaction of triazolinedione with norbornene[75] were found, and the ketone had not reacted.

7,7-Dimethoxybicyclo[2.2.1] heptane. 7,7-Dimethoxybicyclo-[2.2.1] hept-2-ene[50] (14.68 g, 95 mmol) and palladium on carbon (Aldrich, 10%, 0.4 g) were hydrogenated (Parr apparatus). The mixture was filtered through Celite to give 7,7-dimethoxybicyclo [2.2.1.] heptane (12.9 g, 87%) as a clear oil: ir ($CHCl_3$) 2960 (vs), 2730 (s), 1470 (s), 1400 (s), 1330 (s), 1310 (w), 1170 (s), 1140 (m), 1090 (s), 1060 (s), 995 (m), 855 (m), 720 (m, br); NMR ($CDCl_3$) 1.0-2.1 (m, br, 10 H), 2.36 (s, 6 H).

7-Norbornanone. 7,7-Dimethoxybicyclo [2.2.1.]heptane (4.12 g, 26 mmol) in glacial acetic acid was heated to just below reflux for 15 hr. The brown mixture was cooled and transferred to a separatory funnel with 60 mL petroleum ether. The lower part of the funnel was immersed in an ice bath. A solution of 24 g NaOH in 80 mL water was added slowly. The mixture was extracted 3 times with 50 mL portions of petroleum ether. Water (80 mL) was added and the mixture was extracted once more with 50 mL petroleum ether. The ether was dried ($MgSO_4$) and was concentrated to 30 mL by distillation at atmospheric pressure. Recrystallization at -78° gave 7-norbornanone (2.05 g, 74%) as a low melting solid. Recrystallization from petroleum ether gave a solid (425 mg, 15%): mp 90-92° (lit.[50a] mp 77-79°); ir ($CHCl_3$) 2950 (s), 2870 (m), 1835 (vw), 1765 (s), 1740 (m), 1140 (m), 1110 (m), 1070 (m).

7-Norbornylidenenorbornane was prepared by the $TiCl_3$-Li procedure used to prepare adamantylideneadamantane. Rotary evaporation afforded 7-norbornylidenenorbornane (0.95 g, 45%) as an off-white solid: mp 132-136° (lit.[49] mp 137-138°) which was found by GLC (Column A) to be 95% pure.

About 0.5 g crude product was dissolved in 40 mL refluxing absolute methanol. The volume was reduced to 20 mL by boiling and the mixture was allowed to cool, affording white crystals: mp 136-138°, ir ($CHCl_3$) 2940 (s), 2900 (s), 1450 (m), 1395 (w), 1130(M), 860 (w), 830(w); NMR ($CDCl_3$) 1.17-1.24 (m, 8 H), 1.44-1.47 (m, 8 H), 2.32-2.36 (m, 4 H); ^{13}C NMR ($CDCl_3$) 130.99 (quarternary carbon), 36.99 (methine), 29.49 (methylene); mass spectrum 188 (M^+, 29.15).

[2+2] Adduct of 4-Methyl-1,2,4-triazoline-3,5-dione and 7-Norbornylidenenorbornane (34). To a solution of 7-norbornylidene norbornane (100 mg, 0.53 mmol) in 2.5 mL methylene chloride, protected from light and moisture, was added with stirring N-methyl-triazolinedione (60 mg, 0.53 mmol). A bright pink solution resulted. Considerable decolorization occurred within 2 hours; the mixture was stirred at room temperature 12 hr. Evaporation of solvent gave a quantitative yield of a pale pink semisolid. The semisolid was treated with absolute methanol to give white crystals. T wo recrystallizations from methanol gave 34 as a white crystalline solid: mp 140-141.5°; ir ($CHCl_3$) 2960 (s), 2880 (s), 1750 (s), 1700 (vs), 1470 (m), 1465 (m), 1435 (s), 1390 (s), 1365 (w), 1300 (m), 1260 (m), 1130 (m), 1000 (s), 960 (m), 865 (m), 830 (m); NMR ($CDCl_3$) 1.34-1.45 (m, cplx, 8 H), 1.74-1.77 (m, br, 4 H). 2.27-2.31 (m, br, 4 H), 3.06 (s, 3 H); ^{13}C NMR ($CDCl_3$) 159.79 (carbonyl), 90.25 (C adjacent to N), 39.79 (methine), 28.37 (methylene), 28.08 (methylene), 26.04 ($N-CH_3$); mass spectrum 301 (M^+, 1.93), 188 (7.05), 187 (20.00), 186 (20.00).

Anal. Calcd. for $C_{17}H_{23}N_3O_2$: C, 67.75; H, 7.69; N, 10.62. Found: C, 67.43; H, 8.12; N, 13.93.

[2+2] Adduct of 4-Phenyl-1,2,4-triazoline-3,5-dione and 7-Norbornylidenenorbornane (35). To a solution of 7-norbornylidene-norbornane (100 mg, 0.53 mmol) in 4 mL methylene chloride, protected from light and moisture, was added with stirring N-phenyltriazoline-dione (93 mg, 0.53 mmol). The bright red solution was stirred overnight; considerable decolorization had occurred within 1 hr. Evaporation of solvent gave a quantitative yield of an off-white solid. Recrystallization from methanol and washing with ether gave 35 as a white crystalline solid: mp 148-149°; ir ($CHCl_3$) 2960 (s), 2880 (m), 1760 (s), 1700 (vs), 1595 (m), 1500 (m), 1485 (m), 1470 (m), 1465 (m), 1380 (w), 1200 (w), 1120 (m), 1000 (m, br), 830 (w); mass spectrum 363 (M^+), 119 (45.85).

Anal. Calcd. for $C_{22}H_{25}N_3O_2$: C, 72.70; H, 6.93; N, 11.56. Found: C, 72.37; H, 7.38; N, 11.49.

Relative Rates of Reaction of Triazolinedione with 1,3- Cyclohexadiene (Diels Alder) and with 2,3-Dimethyl-2-butene Ene Reaction.

A. In Methylene Chloride Solvent. 2,3-Dimethyl-2-butene (3.00 g, 35.6 mmol) and 1,3-cyclohexadiene (0.147 g, 1.83 mmol) were dissolved in 120 mL methylene chloride. (The concentration of 2,3-dimethyl-2-butene was 0.297 M and the concentration of 1,3-cyclohexadiene was 0.015 M.) A solution of N-methyltriazolinedione (0.028 g, 0.25 mmol) in 12 mL methylene chloride was added dropwise with stirring over 0.5 hr to the olefin solution at room temperature. After the solution decolorized, the solvent was removed by rotary evaporation. The product residue was dissolved in DMSO-d_6, and the mixture was analyzed by 250 MHz NMR. The relative rate of Diels Alder reaction of TAD with 1,3-cyclohexadiene to ene reaction of TAD with 2,3-dimethyl-2-butene was measured by integration and found to be 30 to 1.

Control experiments were performed using a larger excess of 2,3-dimethyl-2-butene to 1,3-cyclohexadiene and higher dilution conditions (2,3-dimethyl-2-butene as 4.00 g, 47.5 mmol, 0.158 M; 1,3-cyclohexadiene as 0.102 g, 1.27 mmol, 0.04 M in 300 mL methylene chloride; TAD as 0.025 g, 0.0044 M in 50 mL methylene chloride. The procedure described above was followed, and the relative reactivity was measured by integration (60 MHz NMR) and found to be 37 to 1.

The "first half" of the reaction was run using 2,3-dimethyl-2-butene (4.006 g, 47.6 mmol, 0.158 M), 1,3-cyclohexadiene (0.102 g, 1.27 mmol, 0.04 M) dissolved in 300 mL methylene chloride and adding a solution of N-methyltriazolinedione (0.0118 g, 0.0044 M) in 23 mL methylene chloride as described above. The relative reactivity was

measured by integration (250 MHz) and was found to be 37 to 1.

B. In Benzene Solvent. 2,3-Dimethyl-2-butene (4.005 g, 47.6 mmol) and 1,3-cyclohexadiene (0.104 g, 1.26 mmol) were dissolved in 300 mL benzene. (The concentration of 2,3-dimethyl-2-butene was 0.16 M and the concentration of 1,3-cyclohexadiene was 0.042 M.) A solution of N-methyltriazolinedione (0.025 g, 0.22 mmol) in 50 mL benzene was added dropwise with stirring over 15 min to the olefin solution at room temperature. After the solution decolorized, the solvent was removed by rotary evaporation. The product residue was dissolved in DMSO-d_6, and the mixture was analyzed by 250 MHz NMR. The relative rate of Diels Alder reaction of TAD with 1,3-cyclohexadiene to ene reaction of TAD with 2,3-dimethyl-2-butene was measured by integration and found to be 100 to 1.

Methoxycarbonyl-2-N-phenylcarbamoyl-4-phenyl-1,2,4-triazolidine-3,5-dione (36).[69] N-phenyltriazolinedione (ca. 200 mg) was dissolved in 10 mL methylene chloride and 2 mL methanol at room temperature. The solution became yellow within 15 min. Evaporation of solvent gave a yellowish solid. Recrystallization from chloroform gave 36 as a white solid: mp 235-236° (lit.[69] mp 180-187°); ir ($CHCl_3$) 3310 (m, br), 1810 (w), 1760 (vs), 1730 (sh), 1600 (s), 1540 (s), 1445 (m), 1435 (m), 1400 (s), 1275 (m), 1200 (w), 1160 (m), 1060 (m), 710 (s), 660 (m); NMR ($CDCl_3$) 4.05 (s, 3 H), 7.15-7.5 (m, 10 H), 9.05 (s, br).

Reaction of 4-Phenyl-1,2,4-triazoline-3,5-dione and 4,4-Dimethyl-2,3-dihydro-γ-pyran.

a. In benzene. To a solution of 4,4-dimethyl-2,3-dihydro-γ-pyran[70] (157 mg, 1.4 mmol) in 7 mL dry benzene, protected from light and moisture, was added N-phenyl triazolinedione (245 mg, 1.4 mmol). The mixture was stirred 4.5 hr at room temperature. Filtration gave a pink solid the [2+2] adduct of 4-Phenyl-1,2,4-triazoline-3,5-dione and 4,4-dimethyl-2,3-dihydro-γ-pyran (263 mg, 65%): mp 148-152° (dec.); ir (KBr) 1765 (m), 1690 (s), 1655 (s), 1475 (s), 1250 (m), 1230 (m); ir ($CHCl_3$) 2960 (m), 1775 (m), 1715 (s), 1595 (w), 1495 (m), 1455 (m), 1385 (s), 1350 (m), 1255 (m), 1210 (m), 1135 (s), 1120 (s), 1030 (s), 1000 (m), 980 (m), 910 (m), 865 (m), 850 (m), 820 (m); NMR ($CDCl_3$) 1.15 (s, 6 H), 1.35-2.55 (m, 2 H), 3.45-4.40 (m, 3 H), 5.85 (d, 1 H, J = 8), 7.50 (s, 5 H); mass spectrum 287 (M^+). NMR (CD_3CN) 1.05 (s, 3 H), 1.08 (s, 3 H), 1.4-2.5 (m, 2 H), 3.5-4.2 (m, 3 H), 5.85 (d, 1 H, J = 8), 7.45 (s, 5 H).

b. In CD_3CN. To a solution of 4,4-dimethyl-2,3-dihydro-γ-pyran (51 mg, 0.45 mmol) in 0.75 mL CD_3CN was added N-phenyl triazolinedione (80 mg, 0.45 mmol), and the reaction was followed by NMR. The initial product was diazetidine. To half the solution was added 100 μL acetone. There was no immediate reaction. After 24 hr, both aliquots were completely converted to vinyl urazole. The conversion of diazetidine to vinyl urazole is slower in CD_3CN solvent than in $CDCl_3$ solvent.

Reaction of Diazetidine (37) with Excess Acetone in Deuteriochloroform

A solution of diazetidine 37 in deuteriochloroform and excess acetone was left at room temperature 24 hr. Solvents were evaporated and the residue was analyzed by NMR, showing only the vinyl urazole.

Reaction of 4-Methyl-1,2,4-triazoline-3,5-dione and 4,4-Dimethyl-2,3-dihydro-γ-pyran.

a. In methylene chloride. To a solution of 4,4-dimethyl-2,3-dihydro-γ-pyran (74 mg, 0.66 mmol) in 3 mL methylene chloride, protected from light and moisture, was added N-methyltriazolinedione (74 mg, 0.66 mmol). The mixture decolorized after stirring 2 hr at room temperature. The mixture was stirred 2 days more, and the solvent was evaporated. The NMR spectrum of the crude product was consistent with the quantitative formation of vinyl urazole product. Recrystallization from 5 mL reagent acetone (concentrated to 2 mL) gave 1-(3-oxa-6,6-dimethylcyclohexenyl)-4-methyl-1,2,4-triazolidine-3,5-dione (55 mg, 37%) as colorless rhombic crystals: mp 172.5-173.5°; ir ($CHCl_3$) 3400-3100 (br), 2960 (s), 1760 (s), 1700 (vs), 1650 (s), 1470 (s), 1395 (m), 1360 (w), 1330 (w), 1200 (s, br), 1165 (w), 1135 (s), 1010 (w), 995 (m), 850 (m), 830 (m); NMR ($CDCl_3$) 1.13 (s, 6 H), 1.75 (t, 2 H), 3.10 (s, 3 H), 4.10 (t, 2 H), 6.68 (s, 1 H), 9.0 (s, br, 1 H); NMR (CD_3COCD_3) 1.15 (s, 6 H), 1.75 (t, 2 H), 3.00 (s, 3 H), 4.10 (t, 2 H), 6.68 (s, 1 H), 9.0 (s, br, 1 H); NMR (CD_3COCD_3) 1.15 (s, 6 H), 1.75 (t, 2 H), 3.00 (s, 3 H), 4.10 (t, 2 H), 6.70 (s, 1 H), 9.0 (s, br, 1 H); mass spectrum 225 (M^+).

Anal. Calcd. for $C_{10}H_{15}N_3O_3$: C, 53.32; H, 6.71; N, 18.66. Found: C, 53.24; H, 6.75; N, 18.61.

b. In benzene. To a solution of 4,4-dimethyl-2,3-dihydro-γ-pyran (58 mg, 0.5 mmol) in 2 mL dry benzene, protected from light and moisture, was added N-methyl triazolinedione 58 mg, 0.5 mmol). A precipitate appeared within 10 min. The stirrer was stopped and the flask was kept

closed for a day. Filtration gave the [2+2] Adduct of 4-Methyl-1,2,4-triazoline-2,5-dione and 4,4-dimethyl-2,3-dihydro-γ-pyran as an offwhite solid (230 mg, 45%), mp 168-171°, accompanied by a few larger chunky crystals: mp 173-175°; ir (KBr) 1765 (m), 1690 (s), 1655 (s), 1475 (s), 1250 (m), 1230 (m); NMR (CD_3COCD_3) 1.02 (s, 3 H), 1.10 (s, 3 H), 1.5-1.9 (m, 2 H), 2.93 (s, 3 H), 4.1-4.3 (m, 3 H), 5.77 (d, 1 H, J = 7); mass spectrum 225 (M^+).

c. In chloroform. 4,4-Dimethyl-2,3-dihydro-γ-pyran and N-methyl triazolinedione were allowed to react (1:1) at room temperature in deuteriochloroform while folloiwng the reaction by NMR. After 10 min, the major product was diazetidine 37 . After 24 hr, the diazetidine had been cleanly converted to vinyl urazole.

d. In acetone-d_6. 4,4-Dimethyl-2,3-dihydro-γ-pyran and N-methyl triazolinedione were allowed to react (1:1) at room temperature in acetone-d_6 while following the reaction by NMR. After 10 min, the main product was diazetidine. After 1.5 hr, the products were found to be oxadiazine, diazetidine, and vinyl urazole (4:2:1). After 3 hr, the products were oxadiazine and vinyl urazole (8:1).

[2+2] Adduct of 4-Phenyl-1,2,4,-triazoline-3,5-dione and 4,4-Dimethyl-2,3-dihydro-γ-pyran. To a solution of 4,4-dimethyl-2,3-dihydro-γ-pyran[70] (157 mg, 1.4 mmol) in 7 mL dry benzene, protected from light and moisture, was added N-phenyl triazolinedione (245 mg, 1.4 mmol). The mixture was stirred 4-1/2 hr at room temperature. Filtration gave a pink solid (263 mg, 65%): mp 148-152° (dec.); ir (KBr) 1765 (m), 1690 (s), 1655 (s), 1475 (s), 1250 (m), 1230 (m); IR ($CHCl_3$) 2960 (m), 1775 (m), 1715 (s), 1595 (w), 1495 (m), 1455 (m), 1385 (s), 1350 (m), 1255 (m), 1210 (m), 1135 (s), 1120 (s), 1030 (s), 1000 (m), 980 (m), 910 (m), 865 (m), 850 (m), 820 (m); NMR ($CDCl_3$) 1.15 (s, 6 H), 1.35-2.55 (m, 2 H), 3.45-4.40 (m, 3 H), 5.85 (d, 1 H, J = 8), 7.50 (s, 5 H); NMR (CD_3CN) 1.05 (s, 3 H), 1.08 (s, 3 H), 1.4-2.5 (m, 2 H), 3.5-4.2 (m, 3 H), 5.85 (d, 1 H, J = 8), 7.45 (s, 5 H); mass spectrum 287 (M^+).

Pentafluoronitrosobenzene.[71] Caution: Some mixtures containing Caro's acid are known to be explosive. Preparation and use of Caro's acid should be conducted in a fume hood behind a safety shield.

Concentrated sulfuric acid (18 M, 12.5 mL, 225 mmol) was cooled to 0° with stirring in a small beaker over an ice-acetone bath. Potassium persulfate (free of lumps) (14.0 g, 52 mmol) was added in small portions over 15 min, keeping the temperature below 5°. The mixture thickened and required manual stirring. Ice-water (150 mL) was put in a 400 mL beaker and was stirred over ice-acetone. With stirring, the concentrated Caro's acid was cautiously added to the ice-water. The mixture was stirred in the cold 15 min. Potassium carbonate (31.5 g, 227 mmol) was gradually added with stirring over ice-acetone until the pH of the mixture was 7. (Caution: addition of potassium carbonate results in vigorous foaming. Care should be taken during the addition to prevent the mixture from foaming out of the container.) The mixture was filtered through filter paper. The filtrate was transferred to an Erlenmeyer flask and was cooled over ice-acetone. With stirring, pentafluoroaniline (Aldrich, 2.0 g, 11 mmol) was added. The mixture became yellow and was stirred in the cold 2 hr after which time TLC (silica/methylene chloride) showed aniline (Rf = 0.5) and a small amount of product (Rf = 0.65). The reaction mixture was stirred in the dark at room temperature 25 hr more. The stirrer had stopped and was coated with a brown residue. A pale blue solid had collected on the neck of the flask and a brown-blue solid had collected at the top of the liquid. These materials were separately

collected and were found by TLC to contain mainly pentafluoronitrosobenzene. The pale blue crop (162 mg, 8%) was identified as pentafluoronitrosobenzene: mp 45-47° (lit.[72] mp 44.5-45°); ir ($CHCl_3$) 1530 (s), 1510 (s), 1490 (s), 1375 (s), 1300 (s), 1110 (vs), 1020 (s). This material was used in kinetic isotope effect studies after purification by sublimation (40°, aspirator vacuum). The blue-brown crop (193 mg, 9%) was found by TLC to contain a second compound beside the desired product.

Pentafluoronitrosobenzene from MCPBA and Pentafluoroaniline. To a heated solution of m-chloroperoxybenzoic acid (Aldrich, 4.45 g, 22 mmol) in 35 mL ethylene dichloride was added a solution of pentafluoroaniline (Aldrich, 2.00 g, 11 mmol) in 20 mL ethylene dichloride. The mixture was heated at reflux 2 hr and became dark brown. After stirring at room temperature 2 days, the mixture was filtered. The filtrate was washed 4 times with 50 mL portions of 1 M NaOH, twice with 50 mL portions of water, and dried ($MgSO_4$). Evaporation under reduced pressure gave a brown oil which was found by TLC (silica/methylene chloride) to contain at least three compounds. Distillation under aspirator pressure afforded pentafluoronitrosobenzene (200 mg, 9%) as a blue oil (bp 80-90°) which formed a low melting solid in the cold: ir ($CHCl_3$) 1630 (m), 1530 (s), 1505 (s), 1490 (s), 1370 (s), 1300 (s), 1270 (m), 1110 (s), 1020 (s).

Kinetic Isotope Effect Studies with Pentafluoronitrosobenzene by NMR. To a solution of deuterioolefin in $CDCl_3$ (ca. 0.2 M) cooled to -10° under argon was added a solution of pentafluoronitrosobenzene (<1 equiv.) in $CDCl_3$ dropwise with stirring. The solution was transferred under argon to a clean, dry NMR tube and was capped under argon. The solutions were immediately analyzed by 250 MHz NMR, and kinetic isotope effects were determined by integration.

N,N'-Bis(p-toluenesulfonyl)Sulfur Diimide was prepared by the method of Singer.[73] N-sulfinyl-p-toluene-sulfonamide (5.00 g, 23 mmol) was dissolved in 5 mL dry benzene under argon. Pyridine (dried over KOH, 100 μL) was added with stirring. Within 5 min, the mixture formed a yellow slurry; 4 mL more benzene was added. The mixture was stirred 6 hr at room temperature and was then filtered, washing the precipitate with a few mL carbon tetrachloride. Drying under high vacuum overnight gave N,N'-bis-(p-toluenesulfonyl) sulfur diimide (3.3 g, 80%) as a yellow solid: mp 40-45° (lit.[73] m.p. 40-45°).

Kinetic Isotope Effect studies with N,N'-Bis-(p-toluenesulfonyl) Sulfur Diimide by NMR. To a solution of deuterioolefin in $CDCl_3$ (ca. 0.4 M) cooled to 0° under argon was added a solution of N,N'-Bis-(p-toluenesulfonyl) sulfur diimide (ca. 1 equiv.) in $CDCl_3$ dropwise with stirring. When the reaction was complete (after 1 hr), the pale green solution was transferred under argon to a dry NMR tube and was capped under argon. The solutions were immediately analyzed by 250 MHz NMR, and kinetic isotope effects were measured by integration.

Dodecadeuterio-2,3-dimethylbutane-2,3-diol was made by literature methods.[74] An oven-dried (120°) 500 mL 3-necked round bottom flask fit with a dry ice condenser, overhead stirrer, and dropping funnel was charged with benzene-washed magnesium turnings (19.34 g, 795 mmol), mercuric chloride (10.8 g, 40 mmol) and 150 mL dry benzene. Hexadeuterio-acetone (15.0 g, 468 mmol) was added with stirring at room temperature. The mixture was gradually heated to reflux over 0.5 hr, and was refluxed 2 hr. After cooling, water (51 mL) was added dropwise with overhead stirring; the mixture was then heated at reflux 1 hr. The overhead stirrer was removed and was replaced with a magnetic stirrer. The supernatant liquid was decanted; 150 mL benzene was added to the remaining solids and the mixture was heated at reflux 1 hr more. The solvent was decanted and the remaining material was filtered and washed with a few mL benzene. The benzene washings were combined with the decanted solvent and were distilled at atmospheric pressure to half the original volume. The liquid was mixed with 55 mL water. Recrystallization gave dodecadeuterio-2,3-diemthylbutane-2,3-diol hexahydrate (18.2 g, 16%) as a white flaky solid.

The solid hexahydrate and 70 mL benzene was refluxed with a Dean-Stark trap until no more water separated. Benzene was evaporated by rotovap, giving an oil with a few suspended particles. The oil was triturated with a few mL pentane and was cooled, giving a low melting solid. High vacuum afforded dodecadeuterio-2,3-dimethylbutane-2,3-diol (6.94 g, 11%).

Dodecadeuterio-2,3-dimethyl-2-butene was made by literature methods.[74] Dodecadeuterio-2,3-dimethylbutane-2,3-diol (6.94 g, 53 mmol) and triethyl orthoformate (7.89 g, 53 mmol) were put in a 25 mL round bottomed flask fit with a Vigreux column and a short path stillhead. The mixture was heated to 140°; liquid (ca. 4 mL) distilled and was collected over dry ice-acetone. A clean column and stillhead were added and 20 mL glacial acetic acid was added to the mixture. The mixture was heated in an oil bath from 160° to 220°; the distillate was collected over dry ice-acetone. Each fraction was analyzed by GLC (Column A). The fractions were combined and washed twice with 4 mL portions of water and dried ($MgSO_4$). Distillation through a micro-distillation apparatus at room temperature afforded dodecadeuterio-2,3-dimethyl-2-butene (700 mg, 14%) as a clear oil: bp 69-73°; ir ($CHCl_3$) 3000 (w), 2220 (s), 2180 (s), 2110 (s), 2060 (s), 1040 (m), 1000 (m), 710 (s).

Competition Reactions of Enophiles Toward a 1:1 Mixture of 2,3-Dimethyl-2-butene-d_o and 2-3-Dimethyl-2-butene-d_{12}.

A. Reaction of 4-Methyl-1,2,4-triazoline-2,5-dione with 2,3-Dimethyl-2-butene d_o and 2,3-dimethyl-2-butene-d_{12}. To a stirred solution of 2,3-dimethyl-2-butene-d_o (Aldrich, Gold Label, 99+%, 31.4 mg 0.373 mmol, 0.0074 M) and 2,3-dimethyl-2-butene-d_{12} (37.2 mg, 0.387 mmol, 0.0077 M) in 50 mL diethyl ether at 0° was added a solution of N-methyltriazolinedione (sublimed at 45-50°, 0.07 Torr, mp 103-104°, 43.0 mg, 0.38 mmol) in 20 mL diethyl ether, with protection from light and moisture. After reaction was complete (corresponding to 50% reaction of total olefin), the resulting mixture was analyzed for unreacted olefin by GC/MS. A kinetic isotope effect k_H/k_D of 1.01 was found.

B. Reaction of 4-Phenyl-1,2,4-triazoline-2,5-dione with 2,3-Dimethyl-2-butene d_o and 2,3-dimethyl-2-butene-d_{12}. To a stirred solution of 2,3-dimethyl-2-butene-d_o (Aldrich, Gold Label, 99+%, 31.4 mg, 0.373 mmol, 0.0074 M) and 2,3-dimethyl-2-butene-d_{12} (37.2 mg, 0.383 mmol, 0.0077 M) in 50 mL diethyl ether at 0° was added N-phenyl triazolinedione (sublimed at 93°, 0.04 Torr, mp 170-175°, 66.0 mg, 0.38 mmol) in 20 mL diethyl ether, with protection from moisture. After reaction was complete, the mixture was analyzed for unreacted olefin by GC/MS. A kinetic isotope effect K_H/k_D of 1.02 was found.

C. Reaction of Pentafluoronitrosobenzene with 2,3-Dimethyl-2-butene d_o and 2,3-dimethyl-2-butene-d_{12}. To a stirred solution of 2,3-dimethyl-2-butene-d_o (Aldrich, Gold Label, 99+%, 31.4 mg, 0.373 mmol, 0.0074 M) and 2,3-dimethyl-2-butene-d_{12} (37.2 mg, 0.387 mmol, 0.0077 M) in 50 mL diethyl ether at 0° was added pentafluoronitrosobenzene (Ventron, mp 45-47° [lit.[72] mp 44.5-45°]), 75 mg, 0.38 mmol) in 20 mL diethyl ether, with protection from moisture. After reaction was complete (2 hr), the mixture was analyzed for unreacted olefin by GC/MS. A kinetic isotope effect k_H/k_D of 1.03 was found.

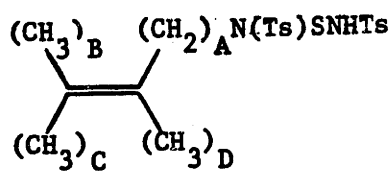
D. Reaction of N,N'-Bis(p-toluenesulfonyl)sulfur diimide with 2,3-Dimethyl-2-butene d_o and 2,3-dimethyl-2-butene-d_{12}. To a stirred solution of 2,3-dimethyl-2-butene-d_o (Aldrich, Gold Label, 99+%, 31.4 mg, 0.373 mmol, 0.0074 M) and 2,3-dimethyl-2-butene-d_{12} (37.2 mg, 0.387 mmol, 0.0077 M) in 50 mL diethyl ether at 0° was added N,N'-bis (p-toluenesulfonyl) sulfur diimide (mp 40-45°, [lit.[73] mp 40-45°]), 141.0 mg, 0.38 mmol) in 40 mL diethyl ether, with protection from moisture. After reaction was complete (2 hr), the mixture was analyzed for unreacted olefin by GC/MS. A kinetic isotope effect k_H/k_D of 1.03 was found.

Table XII. Relative Areas of Products from Reaction of TsNSNTs with Hexadeuterio-2,3-dimethyl-2-butenes.

Olefin	A δ=4.17	B[a] δ=1.73	C[b] δ=1.55	D δ=1.17
Gem A	26	7	7	38
Gem A	91	30	33.7	146.7
Gem B	26	8.5	9	44
Gem B	112.7	34.7	34	172
Cis A	25	24	23	8.5
Cis A	47	49.7	48.7	18
Cis B	19	20	21	7.5
Cis B	77	82	81.7	31.3
Trans A	16	20	22	7
Trans A	64.3	75.7	88	30.7
Trans B	8	11	14	4.5
Trans B	41.7	46.7	55	16.7

[a] B or C.

[b] C or B.



[c] Isotope effects for the gem olefin were calculated by using the expression $k_H/k_D = (1.5\ A + D)/(B + C)$.

[d] Isotope effects for the cis and trans olefins were calculated by solving the overdetermined set of four equations in two variables corresponding to each experiment. B and C were usually consistent; when necessary, B and C were forced to be consistent. The comparable size of areas for B and C demand the loss of stereochemistry in the overall reaction; the formation of equal amounts of the two isomeric products is assumed. The isotope effects obtained by the previously described method are nearly equivalent to those obtained from the expression $k_H/k_D = (1.5\ A)/D$.

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51. The use of GC/MS as a means of measuring the isotope effect in the competition reaction of 2,3-dimethyl-2-butene -d_0 and 2,3-dimethyl-2-butene-d_{12} toward TsNSNTs, TAD, and C_6F_5NO has allowed us to observe the effects of electron impact on the two olefins. Loss of deuteriomethyl occurs more readily than loss of methyl on olefin fragmentatio $k_{CH_3}/k_{CD_3} = 0.94$ or $k_{CD_3}/k_{CH_3} = 1.06$. This effect is in contrast to trends found in hydrocarbons, in which methyl is lost more readily than deuteriomethyl ($k_{CH_3}/k_{CD_3} = 1.3$) in intramolecular competitions with deuterated neopentanes. (Foley, P., Ph.D. Thesis, M.I.T., March, 1979, and references therein.)

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