TLC-pure product.

The activities (μCi/mmol) of the original labeled acid and of the recovered, unsolvolyzed tosylate were determined by liquid scintillation counting (toluene-2,5-diphenyloxazole for tosylates and toluene-2,5-diphenyloxazole-scintisol for *p*-toluenesulfonic acid).

The second-order exchange constants, k_{exc}, were calculated as described earlier for similar experiments.[10]

E. Exchange between *threo*-3-Phenyl-2-butyl *p*-Toluenesulfonate (1) and Sodium *p*-Toluenesulfonate-*4*-^{14}C. In a typical experiment, 50 mL of anhydrous acetic acid (0.1155 M sodium acetate, 0.0120 M sodium tosylate-^{14}C, 0.114 μCi/mmol) was thermostated at 74.8 °C for 1.5 h. At zero time, 1.55 g (4.64 mM) of **1** was added, followed by vigorous shaking for 2 min. After 1.25 h, the reaction was quenched by cooling and the solution was poured into 100 mL of ice water. After crystallization the tosylate was collected by filtration. The ester was dissolved in ether and washed with water and saturated sodium chloride. After drying ($MgSO_4$), recrystallization from ether–hexane gave 0.71 g of **1**.

The activities (μCi/mmol) of the original labeled salt and of the recovered, unsolvolyzed tosylate were determined by liquid scintillation counting.

Isomerization Studies. In a typical experiment, 25 mL of anhydrous acetic acid was thermostated at 25.00 (±0.02) °C for 1 h. At zero time, 0.5281 g (1.58 mM) of **6**-OTs was added, followed by vigorous shaking for 2 min. After 13.50 h, the solution was poured into 50 mL of ice water and the unsolvolyzed ester was isolated as described for the sulfonate oxygen equilibration experiments. Recrystallization of the isolated ester from chloroform–hexane gave 0.250 g of TLC-pure **6**-OTs.

The ester was reduced to the alcohol with sodium naphthalene as described above and the ether extracts were dried ($MgSO_4$) and used without further purification for the GC determinations of the isomeric compositions of the alcohols. These experiments showed that, under conditions of the experiments in Table II, the unsolvolyzed ester contained <0.3% of the erythro isomer.

In control experiments pure **6**-OTs and synthetic mixtures containing 3.3 and 13.4% erythro isomer were recovered from acetic acid and reduced to the alcohol as described for the isomerization studies. As shown by GC, the alcohols contained zero, 2.9, and 11.9% erythro isomer.

Acknowledgment. This work was supported by the National Science Foundation (CHE75-15879).

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Intra- and Intermolecular Cyclization of Olefinic Tosylhydrazones under Acidic Conditions. A Facile Synthesis of Bicyclic Azoalkanes

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Abstract: Tosylhydrazones of olefinic ketones and aldehydes have been observed to undergo a variety of unusual cyclizations under acidic conditions. The intramolecular version of this novel cyclization reaction has been applied in the synthesis of previously unaccessible bicyclo[3.2.1]- and bicyclo[2.2.1]azoalkanes. Of these two bicyclic systems, the less strained [3.2.1] system is formed with the greater ease, and in either system the intramolecular cyclization is favored by more nucleophilic olefins (isopropenyl better than vinyl). Those systems that do not undergo efficient azoalkane formation, either due to excessive ring strain or lack of olefin nucleophilicity, undergo novel intermolecular cyclizations instead. The assignments of structure to these products has been based upon 300-MHz NMR data and an X-ray crystal study of the most unusual of these condensation products, **9**. From this structural information an internally consistent mechanistic framework for the formation of these products has been developed. Thus, while these intermolecular condensation reactions produce a structurally diverse set of products, all of these products seem to originate from an initial cyclization between a molecule of tosylhydrazone and its highly nucleophilic enamine tautomer.

Introduction

During our studies of the photochemical conversion of azoalkanes into peroxides,[1] we have found it necessary to seek new methods for the synthesis of bicyclo[*n*.2.1]azo compounds (**1** in Scheme I).[2] One such approach involved the decomposition of olefinic tosylhydrazone salts under basic conditions. For years this method has provided one of the standard routes to diazoalkanes and the carbenes which frequently arise from the decomposition of these diazo intermediates.[3] It was hoped

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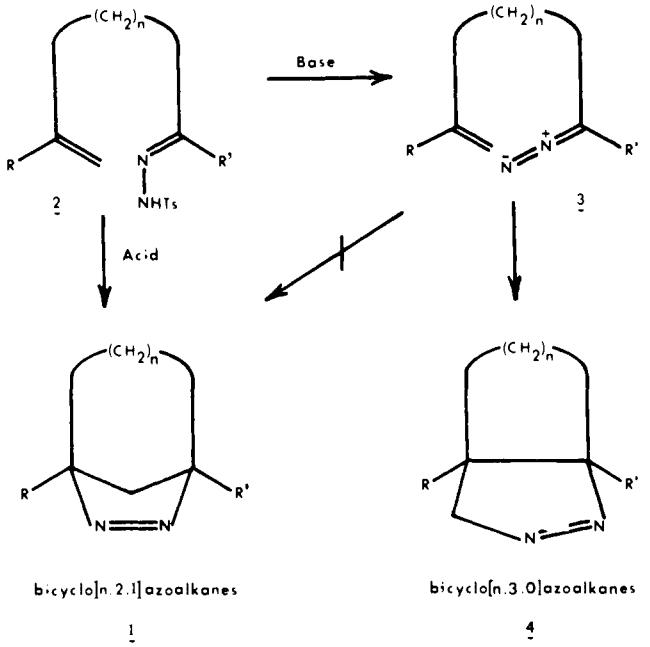
Table I. Methods and Results of Tosylhydrazone Cyclizations

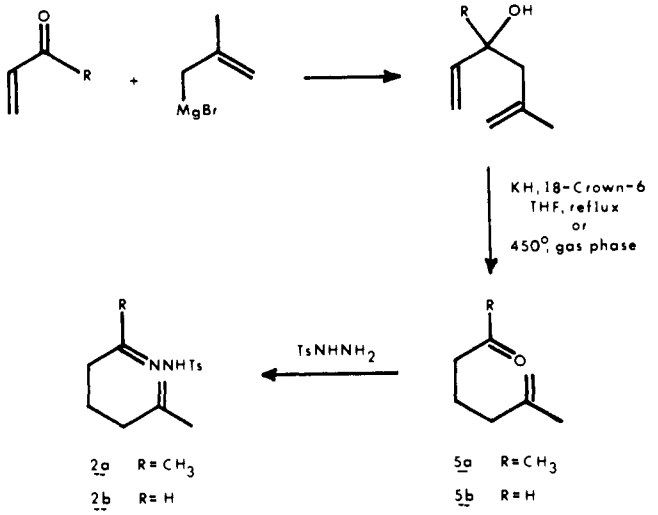
tosylhydrazone	method of tosylhydrazone preparation[a]	cyclization conditions	yields[b] (%)
2a (n = 3; R, R′ = CH_3)	A	$Et_2O{\cdot}BF_3$; CH_2Cl_2; 0 °C–RT; 2.5 h	**1a** (87)
		H_2SO_4; PhH; 60 °C; 1 h	(15)
		TsOH; PhH; 65 °C; 2.5 h	(45–50)
		$AlCl_3$; PhH; RT; 2 h	(65)
2b (n = 3; R = CH_3; R′ = H)	A	$Et_2O{\cdot}BF_3$; CH_2Cl_2; 0 °C; 0.5 h	**1b** (46)
2c (n = 3; R, R′ = H)	B	$Et_2O{\cdot}BF_3$; CH_2Cl_2; 0 °C–RT; 24 h	**1c** (14)
2d (n = 2; R, R′ = CH_3)	C	$Et_2O{\cdot}BF_3$; PhH; reflux; 6 h	**1d** (42), **7** (39)
2e (n = 2; R = CH_3; R′ = H)	B	$Et_2O{\cdot}BF_3$; CH_2Cl_2; reflux; 18 h[c]	**1e** (55)
2f (n = 2; R, R′ = H)	B	$Et_2O{\cdot}BF_3$; variety of conditions	**1f** (0), **8** (36), **9** (38)

[a] The carbonyl compounds used to prepare the tosylhydrazones were obtained as follows: method A, (1) 1,2 addition of allyl Grignard reagents to α,β-unsaturated carbonyl compounds, (2) oxy-Cope rearrangement;[8] method B, pyridinium chlorochromate oxidation of the alcohol;[9] method C, commercially available. [b] All yields are of material isolated. [c] High-dilution conditions used.

Scheme I



Scheme II



that olefinic diazo compounds (**3**) generated in this manner might be trapped to afford the desired azoalkane **1** via an intramolecular 1,3-dipolar cycloaddition reaction (Scheme I). Unfortunately, 1,3-dipolar additions of this type do not proceed well unless the olefin substrate is either highly polarized[4] or incorporated into a strained ring system.[5] Thus, it was not surprising that our initial efforts only confirmed the observations of previous workers,[6] who had found that intramolecular 1,3-dipolar cycloadditions between diazoalkanes and simple olefins proceed in quite low yield and with the undesired regiospecificity to afford bicyclo[n.3.0]azo compounds (**4**) (Scheme I).

During this exploratory phase of our investigation, the effect of Lewis acids upon olefinic diazo compounds (**3**) was examined, and, as might be expected, found to produce the rapid and complete loss of nitrogen with the exclusive formation of hydrocarbon products. However, when the parent olefinic tosylhydrazones (**2**) were treated with acids, an entirely different reaction was observed; little if any hydrocarbon was produced and the desired bicyclo[n.2.1]azo compounds (**1**) often could be isolated from the crude reaction mixtures by a simple trap-to-trap distillation. This surprising reaction provides a new and simple synthesis for previously unaccessible bicyclic azo compounds and represents a fundamentally different and unreported aspect of tosylhydrazone chemistry which may be of use in many other synthetic applications. Therefore, in this paper we report the details of this versatile synthesis of azoalkanes, as well as the structures of several novel bimolecular condensation products. Using the structural information gleaned from these various products, we can begin to provide a mechanistic rationale that accounts for the complexities of olefinic tosylhydrazone chemistry under acidic conditions.

Synthesis of Bicyclo[n.2.1]azoalkanes

The olefinic carbonyl compounds required for the preparation of the tosylhydrazones **2a–f** are readily available (see Table I and Experimental Section). However, the preparation of **2a** and **2b** deserves special comment. In our hands the known method for preparing the methyl ketone **5a** led to mixtures of olefinic isomers.[7] This problem was circumvented by using the oxy-Cope route shown in Scheme II to prepare both **5a** and **5b** free from isomeric olefinic impurities.[8a,b]

Of the tosylhydrazones listed in Table I, **2a** was studied most thoroughly. Its cyclization to **1a** was found to proceed readily with a wide variety of protic and Lewis acids. The more successful conditions are noted in Table I. Boron trifluoride proved to be the most generally applicable acid.

As indicated in Table I, the tosylhydrazones in the n = 3 series (**2a–c**) afforded the azoalkanes under milder conditions than those in the n = 2 series (**2d–f**), and in general yields of the [3.2.1]azoalkanes seemed to be significantly higher than those of the more strained [2.2.1]azoalkanes. Furthermore, there is a distinct tendency for methyl substitution of the olefin moiety to improve the yields of the cyclization to the azoalkane. This effect is probably due to the enhanced nucleophilicity imparted to the olefin by methyl substitution and to the electrophilic nature of the tosylhydrazone-derived species which attacks the olefin (vide infra). Indeed the combination of increased ring strain and reduced olefin nucleophilicity apparently is sufficient to inhibit completely the formation of azoalkane **1f**.[10] In contrast, an essentially quantitative yield is

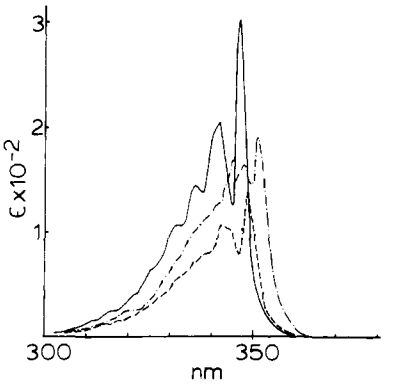


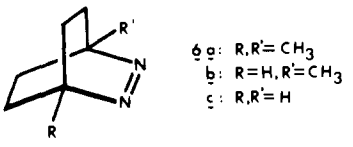
Figure 1. n,π* absorption band of 6,7-diazabicyclo[3.2.1]oct-6-enes **1a–c**: **1a**, -·-; **1b**, - - -; **1c**, —.

obtained in the case of azoalkane **1a.** Here the isolated yield of **1a** is reduced to 87% by losses incurred during the removal of solvent from this extremely volatile substance. The isolated yields for the other azoalkanes are reduced even more by this solvent removal problem; however, in these cases the reduction in azoalkane yields also can be traced to the formation of bimolecular condensation products. The formation of these condensation products is more troublesome in the $n = 2$ series and in those cases with unsubstituted olefins. In attempts to suppress formation of the bimolecular products, high-dilution reaction conditions were examined. However, the greater volumes of solvent involved only aggravated the product entrainment problem with the result that the isolated yields of azoalkanes were not always improved by high-dilution reaction conditions.

Finally, a considerable amount of effort has been devoted to structural studies of the $n = 2$ bimolecular condensation products, and this work is described in a subsequent section.

Electronic Absorption Spectrum of the Bicycloazoalkanes

Owing to the recent interest in the electronic absorption properties of azoalkanes,[11] and since the most characteristic spectral property of the azoalkanes synthesized in this work is their n,π* absorption bands, we have recorded these data in Figures 1 and 2 and Table II. The same general behavior is exhibited in both the bicyclo[3.2.1] series (**1a–c,** Figure 1) and in the bicyclo[2.2.1] series (**1d–f,** Figure 2). In both series there is a distinct bathochromic shift and hypochromic effect associated with the introduction of the bridgehead methyl groups. We are not certain as to the origin of this effect. However, it is interesting to note that the analogous bicyclo[2.2.1] series (**6a–c,** Table II) displays the same bathochromic shift, but does



not exhibit any significant variation in band intensity with bridgehead methyl substitution.[11,12]

Structures of the Bimolecular Condensation Products

In order to gain a better understanding of the mechanistic aspects of the acid-mediated condensations of olefinic tosylhydrazones, a substantial effort has been devoted to the determination of the structures of the intermolecular condensation products. The products formed in the reactions of **2d** and **2f** have been studied in the greatest detail.

In the reaction of the tosylhydrazone **2d** the azoalkane **1d** is formed along with a much less volatile intermolecular condensation product **7**. This material has an empirical formula of $C_{14}H_{24}N_2$ and is a dialkylhydrazone (>C=NNR$_2$) as

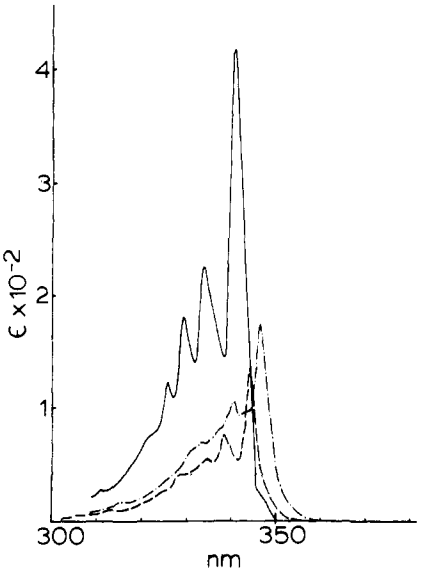


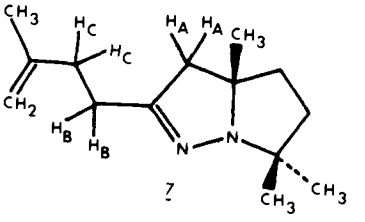
Figure 2. n,π* absorption band of 2,3-diazabicyclo[2.2.1]hept-2-enes **1d–f**: **1d**, -·-; **1e**, - - -; **1f**, —.

Table II. Electronic Absorption Properties of Bicyclic Azoalkanes

bicyclo azoalkanes	λ_{max}, nm (ϵ)[a]		
	R, R' = CH_3	R = H; R' = CH_3,	R, R' = H
[2.2.2]	**6a** 383 (192)[b]	**6b** 380 (200)[c]	**6c** 377 (193)[b]
[3.2.1]	**1a** 351 (192)	**1b** 349 (140)	**1c** 347 (305)
[2.2.1]	**1d** 347 (174)	**1e** 344 (135)	**1f** 341 (420)[b]

[a] Spectra determined in *n*-pentane unless noted otherwise. [b] Spectrum determined in hexane, ref 11. [c] Spectrum determined in hexadecane, ref 12.

judged from infrared data (>C=N-, 1644, cm^{-1}, no >NH). The loss of -CH_3 and -$CH_2C(=CH_2)CH_3$ gives rise to the major fragments in the mass spectrum of **7**. The 300-MHz



7

NMR spectrum (δ, $CDCl_3$) of **7** displays four methyl singlets: one at 1.77 ppm, >C=CCH_3; two as a single peak at 1.32 ppm, which is separated into two singlets when the spectrum is taken in 1:1 C_6D_6-$CDCl_3$, >NCCH_3; and finally one at 1.16 ppm, >NCCH_3.[13] In addition three allylic methylene patterns are clearly discernible: AB system, J = 17 Hz, 2.47 and 2.69 ppm, H_A; overlapping doublet of triplets, J = 5 and 7 Hz, 2.43 ppm, H_B; doublet of doublets, J = 7 and 8 Hz, 2.25 ppm, H_C. These data and the subsequently evolved mechanistic considerations are only consistent with the structure **7**.

Reaction of tosylhydrazone **2f** under a variety of conditions produced no azoalkane **1f**, but instead afforded two intermolecular condensation products, **8** and **9** (Table I). The structurally more simple of these, **8,** was an oil which had an empirical formula of $C_{10}H_{14}N_2$. Spectroscopic examination indicated that this substance was a disubstituted pyrazole: ν_{max} (neat) 3600–2500 and 1645 cm^{-1}; λ_{max} (EtOH) 222 nm (log ϵ 3.65); NMR ($CDCl_3$, δ) 7.27 (1 H, s) and 10.18 ppm (1 H, bs). These data are consistent with substitution in the 3 and 4 ring positions; 3,4-dimethylpyrazole has λ_{max} (EtOH) 223

Table III. Chemical Shifts, Coupling Constants, and Dihedral Angles for the Tricyclic Hydrazine **9**

proton no.	chemical shift, δ ppm	coupling constant, Hz	dihedral angle, deg
9′	1.07	$J_{9',9} = 12$; $J_{9',6} = 2.5$; $J_{9',1} = 0$	78.6 (9′,1)
2	1.28	$J_{2,3} = 3$; $J_{2,1''} = 7$; $J_{2,1'} = 7$; $J_{2,1} = 0$	86.3 (2,1)
4′ or 5′	1.60	$J = 4.5$; $J = 11.5$; $J = 11.5$; $J_{5',6} = 0$	82.4 (5′,6)
4′ or 5′	1.79	$J = 5.0$; $J = 11.5$; $J = 11.5$; $J_{4',3} = 0$	89.2 (4′,3)
4	1.94	$J_{4,3} = 6.5$; $J = 5$; $J = 11.5$	
5 and 1′	2.11	$J_{5,6} = 7.5$; $J = 4$	
9 and 1″	2.29	$J_{9,9'} = 12$; $J_{9,6} = 12$; $J_{9,1} = 5$; $J_{1'',2} = 7$	
3	3.06	$J_{3,2} = 3.0$; $J_{3,4} = 6.5$; $J_{3,4'} = 0$	89.2 (3,4′)
6	3.73	$J_{6,9'} = 2.5$; $J_{6,5} = 7.5$; $J_{6,9} = 12$; $J_{6,5'} = 0$	82.4 (6,5′)
1	4.29	$J_{1,9} = 5$; $J_{1,9'} = 0$; $J_{1,2} = 0$	78.6 (1,9′)
			86.3 (1,2)

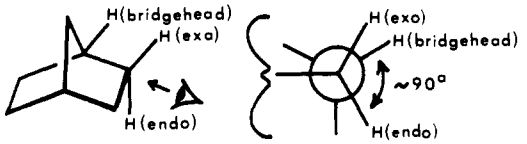
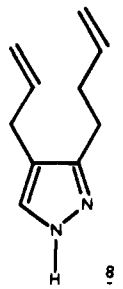


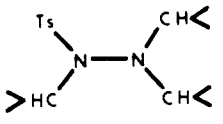
Figure 3. Dihedral angle between bridgehead and bridge protons in bicyclo[2.2.1]heptanes.



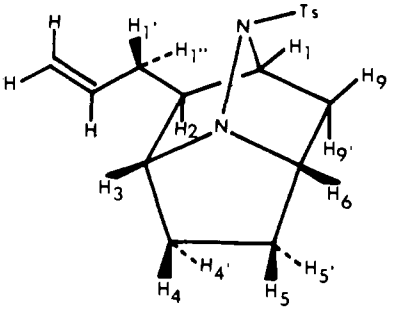
8

nm (log ϵ 3.62)[14] and an NMR signal (δ) at 7.26 ppm for the ring proton at the 5 position.[15] Furthermore, NMR data indicates that the ring substituents are 3′-butenyl and 2′-propenyl groups. Finally, the attachment of the butenyl groups at the 3-ring position and the propenyl group at the 4-ring position is based upon mechanistic considerations (vide infra).

Of particular interest was the much more complex substance **9** which was also obtained from the reaction of **2f.** This substance is a well-defined crystalline material with an empirical formula of $C_{17}H_{22}N_2O_2S$. From the NMR spectrum it was apparent that the substance had a 2′-propenyl group and had retained the tosyl group. Extensive 300-MHz NMR decoupling data[13] indicated that the substituents mentioned above were attached to a tricyclic skeleton containing a trisubstituted tosylhydrazine of the following part structure.



Unfortunately there are several tricyclic structures which might reasonably account for the decoupling data summarized in Table III. Consequently, a single-crystal X-ray study (see the following section) was required in order to unequivocally establish the structure as **9**. With these X-ray results in hand it becomes possible to assign the 300-MHz NMR signals as indicated in Table III. The only ambiguities in analyzing this spectrum arise from the overlap of the signals from protons 5 and 1′ and 9 and 1″ and from the uncertainty in the assignments for protons 4′ and 5′. All geminal and vicinal coupling constants can be observed with four exceptions (Table III): $J_{1,9'}$, $J_{5',6}$, $J_{3,4'}$, and $J_{1,2}$. It was the complete absence of these coupling constants that led to uncertainty in the interpretation



9

of the NMR data. This lack of coupling between bridgehead protons and endo-bridge protons is consistent with observations in simpler bicyclo[2.2.1]heptane systems.[16] As indicated in Figure 3, coupling constants of this type are minimal owing to the approximately 90° dihedral angle that exists between the protons involved. Reference to the X-ray data indicates that the dihedral angles associated with the four missing coupling constants in the spectrum of **9** are all close to 90° (see Table III).

X-ray Structure Determination of 9

An unequivocal structure assignment for the tricyclic hydrazine **9** played a crucial role in the development of a mechanistic description of these tosylhydrazone cyclizations (see following section). This structure was obtained without difficulty by X-ray crystallography, and is illustrated in Figure 4. Atomic positions from the final refinement are available in Table A[17] and bond lengths and angles calculated therefrom appear in Table B. Root mean square displacements are given in Table C, and anisotropic thermal parameters are available as Table D. Attempts to determine the enantiomer present in the actual acentric crystal studied were unsuccessful, presumably owing to the occurrence of a nearly zero value for the y coordinate of the sulfur atom, sulfur being the only atomic species in the molecule with significant anomalous scattering.

All of the bond lengths are quite normal except for the vinyl bond, which is somewhat shorter, 1.256 (7) Å, than would be anticipated. The ring strain in the tricyclic system is evidenced by the considerable distortions from the expected tetrahedral values of many of the bond angles. The seven-membered ring, C_1, C_2, C_3, C_4, C_5, C_6, and C_9, is opened out along a line through C_3 and C_6, giving rise to ring angles C_2, C_3, C_4 of 114.3° and C_5, C_6, C_9 of 115.9°. The other ring angles are considerably less than the tetrahedral values, averaging 102.9°. Likewise, the tosyl group is positioned to reduce its interaction with C_6 and C_9. Thus the C_1, N_8, S_{10} angle opens to 126.6° and the N_7, N_8, S_{10} angle is 120.3°. The solid is composed of isolated molecules with all intermolecular van der Waals contacts appearing quite normal.

If one assumes that the tosyl group is anti with respect to the

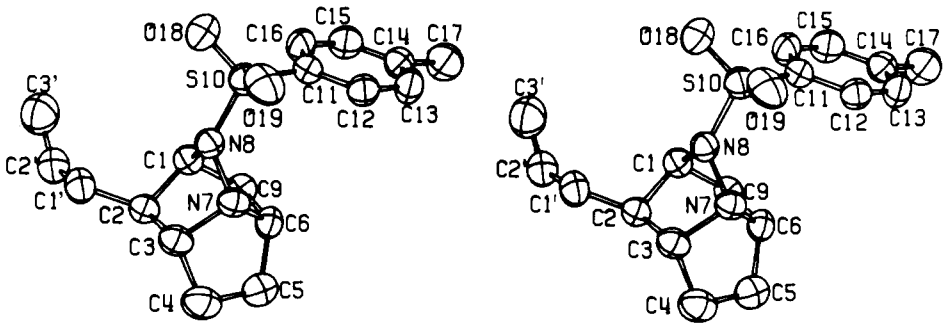


Figure 4. Stereodiagram showing the structure of **9**. Hydrogen atoms have been omitted for clarity.

propenyl group in solution as it is in the crystal (Figure 4), the downfield chemical shifts of certain protons in the NMR spectrum of **9** can be rationalized. Thus, $H_{9'}$ gives rise to a signal at approximately the expected chemical shift, 1.07 ppm (δ). In contrast, H_9 which is attached to the same carbon atom gives rise to a signal at 1.22 ppm lower field, 2.29 ppm. This large difference in chemical shifts seems to be most easily explained as being due to a deshielding of H_9 by the tosyl group. The relative chemical shifts of the three >NCH protons, H_1, H_3, and H_6, also appear to be governed by the tosyl group. The most deshielded of these three is H_1, 4.29 ppm. This is easily understood since this is the only one of the three attached to carbon bearing a tosylamide, $TsNCH_1$. The other two protons, H_3 and H_6, should have very similar magnetic environments. Thus, the downfield chemical shift of H_6 (3.73 ppm) relative to that of H_3 (3.06 ppm) is probably due to the tosyl group deshielding the closer of the two, H_6.

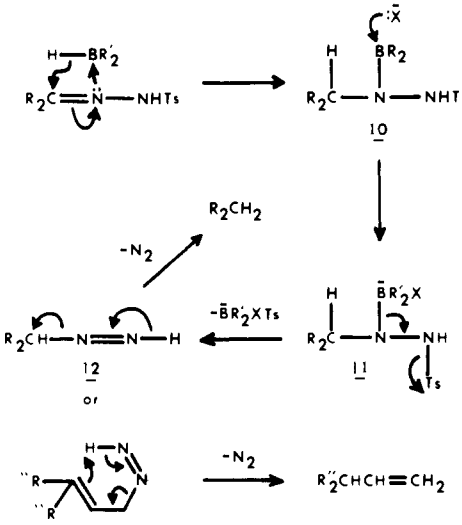
Mechanistic Considerations

The mechanistic details of the azoalkane formation and the intermolecular condensation reactions are particularly interesting, since almost nothing is known about the chemistry of tosylhydrazones under acidic conditions. Those few cases of reactions under acidic conditions which have been examined all deal with the treatment of tosylhydrazones with borane reducing agents (Scheme III).[18] The boranes add to the imine double bond to form aminoboranes (**10**) which upon attack by nucleophilic species (X:) form aminoborates (**11**). Loss of a complex tosylborate salt through a β-elimination leads to alkyldiimides (**12**). These labile species either lose nitrogen directly[18a,b] or undergo retrograde ene reactions to afford rearranged olefins[18c] (see Scheme III).

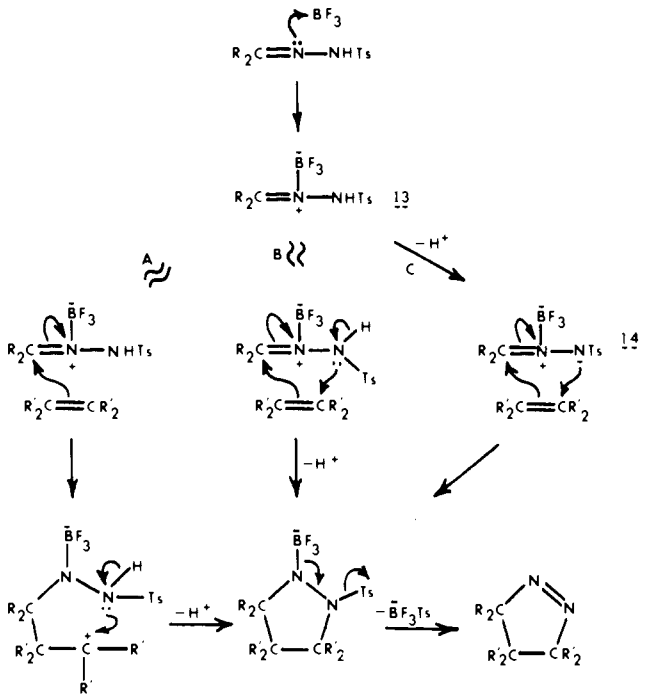
The examples upon which Scheme III is based serve to illustrate the mechanistic events that occur following addition to the imine double bond. However, in the present study the crucial question is how this initial addition to the imine double bond occurs. Two possible mechanistic extremes for the reaction of a tosylhydrazone imminium salt (**13** in Scheme IV) with an olefin have been considered: pathway (a), a stepwise carbocation addition to the olefin followed by the loss of a proton, and pathway (c), a prior loss of a proton followed by a 1,3-dipolar cycloaddition of the resulting azomethine imine **14** to the olefin. Pathway (b) represents an intermediate route between the two extremes, pathways (a) and (c), and in this route the proton is lost during the cyclization reaction with the olefin. Thus, Scheme IV displays a continuum of mechanistic possibilities which vary in the timing with which a proton is lost relative to the cyclization process. The final step in the azoalkane formation outlined in Scheme IV, the elimination of tosylborate ion, is well documented.[18b]

Based upon the following observations it seems unlikely that the 1,3-dipolar cycloaddition extreme, pathway (c), is functioning in these reactions. In the related intramolecular 1,3-dipolar cycloaddition reactions of the azomethine imine **15** (Scheme V) other workers[19] have found that vinyl groups serve quite well as substrates for the dipolar additions. In contrast, vinyl groups do not serve as good substrates for the species involved in the tosylhydrazone cyclizations (**2c** and **2f** in Table I). Only when the olefin bears a methyl substituent does cyclization proceed efficiently. The azomethine imine **15c** forms

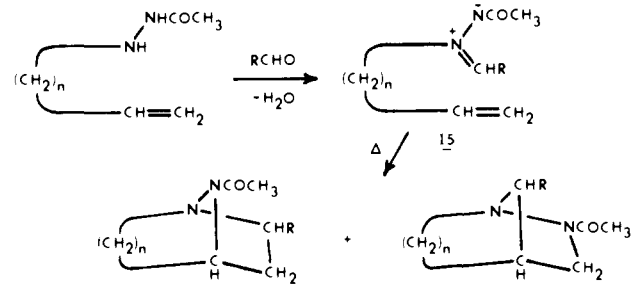
Scheme III



Scheme IV



Scheme V



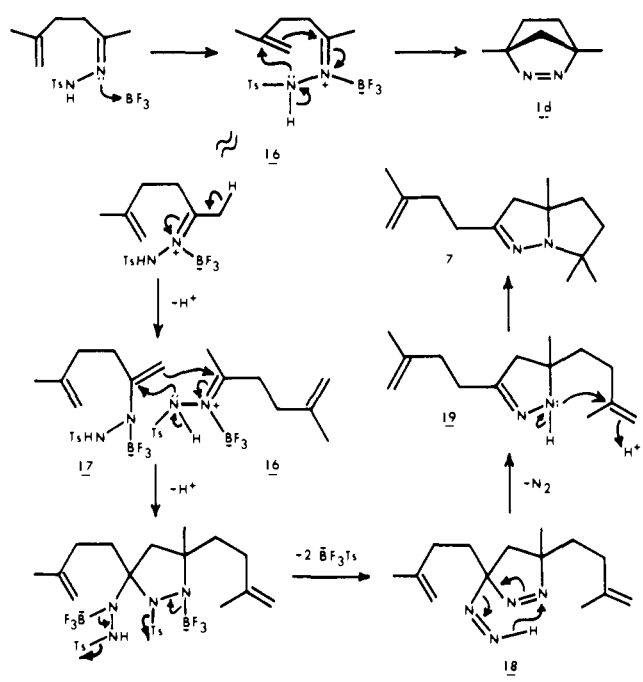
15			
a	R=H, n=3	–	69%
b	R=Ph, n=3	5%	8%
c	R=H, n=2	40%	–

a strained bicyclo[2.2.1] system without difficulty, whereas the species involved in the tosylhydrazone reactions do not (**2f** in Table I). This may be due to the formation of byproducts via enamine intermediates (vide infra), the analogues of which are not available in the series to which **15** belongs. The final and perhaps most convincing argument against the dipolar addition pathway (c) is the failure to observe both modes of addition to the olefin leading to products of type **1** and **4** (Scheme I). All of the tosylhydrazone cyclizations observed to date have proceeded in a completely regiospecific manner to yield the products expected of carbocation cyclizations. In contrast the series of intramolecular azomethine imine dipolar additions shown in Scheme V display a distinct lack of regiospecificity.[19] Consequently, it seems more reasonable to view these tosylhydrazone cyclizations as proceeding through carbocation mechanisms of the type outlined in pathways (a) or (b) of Scheme IV. At present, it is not possible to refine this mechanism further. However, for the remainder of this paper the mechanism outlined in pathway (b) will be used, since it is more economical in the number of steps required.

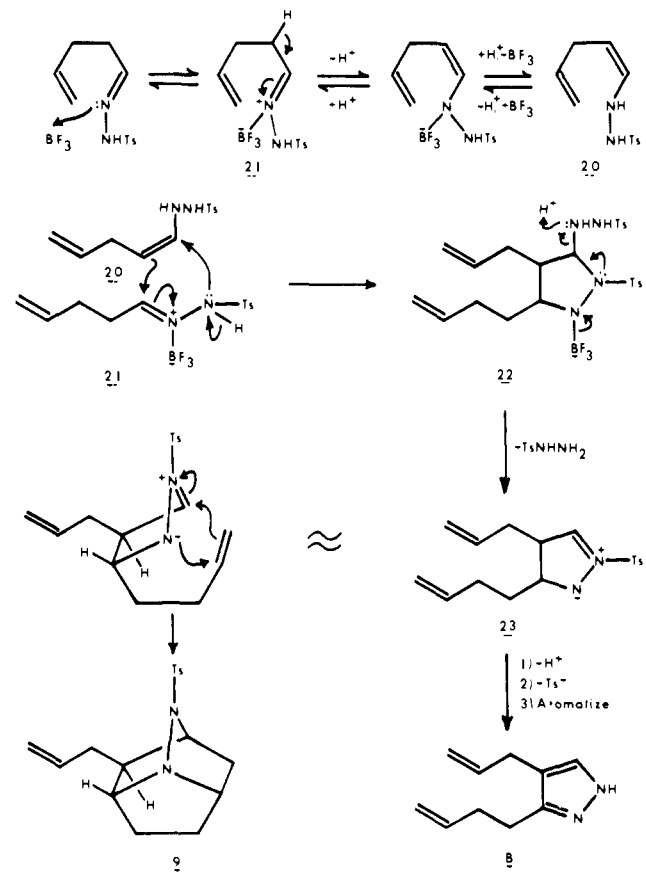
It remains to explore the mechanistic origins of the bimolecular condensation products **7**-**9** and to determine the mechanistic relationship of these products to the azoalkanes. Scheme VI outlines a possible mechanism for the formation of the azoalkane **1d** and the hydrazone **7**. The common intermediate in both processes is the tosylhydrazone complex **16**. Cyclization of **16** as described previously (path (b), Scheme IV) would lead to azoalkane **1d.** Alternatively, **16** might undergo loss of a proton to form the enamine **17**. Any factors which tend to reduce the rate of intramolecular cyclization probably would favor enamine formation. Since more strain is involved in the formation of bicyclo[2.2.1] systems than in the formation of bicyclo[3.2.1] systems, the olefinic tosylhydrazones that give rise to the former would be expected to produce relatively larger amounts of enamines. Once formed enamines such as **17** should provide a highly nucleophilic double bond for reaction with the highly electrophilic tosylhydrazone complex **16**. Thus, the reaction of **16** with **17** would be an intermolecular version of the intramolecular cyclization which leads to the bicyclic azoalkanes. This intermolecular reaction would afford the azoalkane **18** in which the azo and diimide groups are ideally situated for a retrograde ene reaction.[18c] The formation of hydrazone **7** would conclude with the unexceptional acid-catalyzed amine alkylation shown in Scheme VI.

The most important aspect of the mechanism outlined in Scheme VI is the formation and involvement of an enamine species in these intermolecular condensations. Very similar enamine species seem to be required for the formation of condensation products **8** and **9** (Scheme VII). In this case the enamine which results (**20**) is of necessity formed by loss of a methylene proton, whereas in the previous case the enamine **17** has formed by loss of a methyl proton. It is this difference

Scheme VI



Scheme VII



in the regiospecificity of enamine formation that is largely responsible for the variations in the mechanisms outlined in Schemes VI and VII. Thus, in the case of the mechanism shown in Scheme VII, condensation between enamine **20** and the tosylhydrazone complex **21** results in the five-membered diaza heterocycle **22** in which the olefinic side chains are on adjacent carbon atoms. In this instance the tosylhydrazine group is not lost in a reductive process such as that described in Scheme VI, but instead undergoes a simple elimination to yield tosylhydrazine which may be easily isolated from the

reaction mixture. The azomethine imine that results (**23**) either might undergo loss of toluenesulfinic acid followed by aromatization of the five-membered ring to form pyrazole **8**, or, if the relative stereochemistry of the olefinic side chains of **23** is trans, might undergo an intramolecular 1,3-dipolar cycloaddition or a related cationic stepwise annelation to form the tricyclic hydrazine **9**.

Conclusions

The treatment of olefinic tosylhydrazones with acid has been found to lead to a variety of novel cyclization reactions. The most useful of these is the intramolecular cyclization to form bicyclo[*n*.2.1]azoalkanes that are not available by other synthetic routes. In competition with azoalkane formation are bimolecular condensation reactions. These bimolecular processes all seem to involve the reaction of a tosylhydrazone with one of its enamine tautomers. All of these reaction sequences are concluded by a series of eliminations in which toluenesulfinic acid, nitrogen, or tosylhydrazine are lost. The factors which govern these latter steps are still unclear.

Finally, this acid-mediated condensation between a tosylhydrazone functional group and an olefin constitutes a new mode of tosylhydrazone chemistry which should complement the more conventional chemistry of tosylhydrazones under basic conditions. As an indication of the synthetic promise of this method, it has been applied here in the synthesis of previously unknown bicyclo[3.2.1]azoalkanes represented by the parent system **1c.**

Experimental Section

General Procedures. Melting points were determined with a Mettler FP-2 hot-stage apparatus. Nuclear magnetic resonance spectra were recorded with Varian Associates T-60 and 300-MHz spectrometers. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Infrared spectra were recorded with a Perkin-Elmer Model 599 spectrophotometer. Ultraviolet spectra were determined with a Cary Model 14 spectrophotometer. Mass spectra were determined with a Hitachi RMU-7 spectrometer at 70 eV. Gas chromatographic separations were done with a Varian Aerograph Model 90-P instrument. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Thick layer chromatography was performed with EM silica gel 60 F_{254} precoated plates, and column chromatography with EM silica gel (less than 0.08 mm). Unless stated otherwise, drying of moist solutions was done with K_2CO_3 and the removal of solvents was conducted with a rotary evaporator at aspirator pressure.

Preparation of Allylic Alcohols. Methallylmagnesium chloride was prepared in the usual fashion in ethereal solution with equivalent amounts of powdered magnesium and methallyl chloride. To this Grignard solution was added with stirring an ethereal solution of about 1 equiv of either methyl vinyl ketone or freshly distilled acrolein. After stirring for an additional 0.5–1 h the reaction mixture was quenched with aqueous NH_4Cl and extracted with ether, and the ether layer was dried and concentrated under reduced pressure at 15–20 °C. The concentrate was distilled to afford the appropriate allylic alcohol.

3,5-Dimethyl-1,5-hexadien-3-ol: 35%; bp 40 °C (8 mm) (lit.[20] 46–47 °C (10 mm)); IR (neat) 3440, 1637 cm^{-1}; NMR (δ, $CDCl_3$) 1.29 (3 H, s), 1.84 (3 H, bs), 2.29 (2 H, s), 4.75, 4.92, 5.09, and 5.35 (4 H, complex), 6.00 ppm (1 H, dd, J = 10 and 17 Hz).

5-Methyl-1,5-hexadien-3-ol: 43%; bp 64–66 °C (20 mm) (lit.[8b] 145 °C (1 atm)); IR (neat) 3400, 1645 cm^{-1}; NMR (δ, $CDCl_3$) 1.76 (3 H, m), 1.9–2.4 (3 H, m), 4.0–4.5 (1 H, bm), 4.69, 4.83, and 4.95–5.15 (4 H, m), 5.90 ppm (1 H, ddd, J = 10, 15, and 17 Hz).

Oxy-Cope Rearrangement. A. Low-Temperature Method. Preparation of 6-Methyl-6-hepten-2-one (5a). To a solution of 14.38 g (54.4 mmol) of 18-crown-6 and 10.00 g (79.4 mmol) of 3,5-dimethyl-1,5-hexadien-3-ol in 300 mL of anhydrous THF under a nitrogen atmosphere was added 13.93 g of 24.5% KH suspended in mineral oil (85 mmol). The resulting dark orange solution was refluxed for 1 h, cooled, and quenched with 150 g of ice. Following saturation of the aqueous layer with NaCl, the reaction mixture was extracted with ether (3 × 100 mL). The combined organic layers were washed with water (100 mL) and dried, and the solvent was removed at 5–10 °C. The dark yellow residue was distilled to afford 6-methyl-6-hepten-2-one (**5a**): bp 49–50 °C (8.5 mm) (lit.[8b] 149 °C (1 atm)); 7.79 g (61.8 mmol, 78%); IR (neat) 1713 cm^{-1}; NMR (δ, $CDCl_3$) 1.4–2.7 (6 H, m), 1.72 (3 H, m) 2.13 (3 H, s), 4.70 ppm (2 H, bs).

The advantage of this method is that it affords a single olefin isomer. In our hands another method reported to yield this substance afforded it in mixtures of related olefin isomers.[7]

The same isomerically pure ketone also may be obtained by a simple gas-phase pyrolysis over glass wool at 450 °C.[8b,21] However, the yields realized by this procedure are considerably lower (32%) than those obtained by this low-temperature method.

B. High-Temperature Method. Preparation of 5-Methyl-5-hexenal (5b). Neat 5-methyl-1,5-hexadien-3-ol (3.861 g, 34.5 mmol) was pyrolyzed in the vapor phase by dropping (3 drops/min) into a column (1 × 20 cm) packed with glass wool at 450 °C and under 20 mm pressure.[21] The crude yellow pyrolysate was concentrated under reduced pressure at 0 °C to remove acrolein and isobutylene from the oil. The resulting crude 5-methyl-5-hexenal[8b] (**5b**, 1.738 g, 85% pure by NMR, 13.2 mmol, 38%) was used without further purification. The crude aldehyde had IR (neat) 1720 cm^{-1}; NMR (δ, $CDCl_3$) 1.69 (3 H, bs), 1.3–2.6 (6 H, m), 4.65 (2 H, bs), 9.68 ppm (1 H, t, J = 15 Hz).

Pyridinium Chlorochromate Oxidation of Alcohols to Aldehydes. The alcohol was added to a stirred suspension of 1.5–2.5 molar equiv of pyridinium chlorochromate[9] and 0.5–1.0 molar equiv of sodium acetate in 50 mL of anhydrous CH_2Cl_2. After the mixture was stirred for 1.5–4.0 h, 150 mL of ether was added and the solvent decanted from the black residue that had formed. This black residue was washed with ether (4 × 40 mL), the combined extracts were filtered through silica gel–Celite (1:1), and the solvent was removed by distillation through a Vigreux column. Distillation of the residual oil afforded the desired aldehydes.

5-Hexenal: from 5-hexen-1-ol (Chemical Samples Co.); 47%; bp 39–41 °C (245 mm) (lit.[22] 120–121 °C (1 atm)); IR (neat) 2725, 1725 cm^{-1}; NMR (δ, CCl_4) 1.5–2.6 (6 H, m), 4.85 and 5.10 (2 H, m), 5.45–6.15 (1 H, m), 9.72 ppm (1 H, t, J = 1 Hz).

4-Methyl-4-pentenal: from 4-methyl-4-penten-1-ol (Chemical Samples Co.); 32% Kugelrohr distillation (lit.[22] 128 °C (1 atm)); IR (neat) 2735, 1730 cm^{-1}; NMR (δ, $CDCl_3$) 1.72 (3 H, d, J = 1 Hz), 2.05–2.85 (4 H, m), 4.7 (2 H, m), 9.71 ppm (1 H, t, J = 1 Hz).

4-Pentenal: from 4-penten-1-ol (Chemical Samples Co.); 56%; bp 100–105 °C (1 atm) (lit.[23] 102–104 °C); IR (neat) 1720, 1638 cm^{-1}; NMR (δ, $CDCl_3$) 2.3–2.6 (4 H, m), 4.8–6.2 (3 H, m), 9.74 ppm (1 H, t, J = 1 Hz).

Preparation of Tosylhydrazones from Methyl Ketones. The methyl ketone was added to a stirred suspension of about 1.1 equiv of tosylhydrazine and 1 drop of acetic acid in *n*-pentane. Upon stirring for 24 h the solid was collected by filtration and washed with *n*-pentane. A single recrystallization from EtOH at −78 °C afforded the tosylhydrazones as a mixture of syn and anti isomers (ca. 1:9). Material at this level of purity was used in the subsequent cyclizations to the azoalkanes. Analytical samples of the anti isomers were obtained by two further recrystallizations from ether.

6-Methyl-6-hepten-2-one tosylhydrazone (2a) was obtained in 90% yield following recrystallization from EtOH and an analytical sample had mp 81.5–82.5 °C; IR (KBr) 3220, 1645, 1593, 1340, 1168 cm^{-1}; NMR (δ, $CDCl_3$) 1.2–2.4 (6 H, m), 1.65 (3 H, bs), 1.78 (3 H, s) anti [1.91 (s) syn], 2.44 (3 H, s) 4.53–4.80 (2 H, m), 7.32 (2 H, d, J = 8 Hz), 7.90 (2 H, d, J = 8 Hz), 7.5–8.3 ppm (1 H, b). Anal. ($C_{15}H_{22}N_2SO_2$) C, H, N.

5-Methyl-5-hexen-2-one tosylhydrazone (2d) was obtained in 77% yield following recrystallization from EtOH and an analytical sample had mp 108.0–108.5 °C; IR ($CHCl_3$) 3210, 1647, 1597, 1335, 1170 cm^{-1}; NMR (δ, $CDCl_3$) 1.60 (3 H, bs), 1.77 (3 H, s) anti [1.88 (s) syn], 2.0–2.6 (4 H, m), 2.42 (3 H, s), 4.57 (2 H, bs), 7.28 (2 H, d, J = 8 Hz), 7.86 (2 H, d, J = 8 Hz), 7.5–8.4 (1 H, b). Anal. ($C_{14}H_{20}N_2SO_2$) C, H, N.

Preparation of Tosylhydrazones from Aldehydes. The aldehyde was added over 0.5–1.0 h to a stirred suspension of about 1.05 equiv of tosylhydrazine in *n*-pentane at 0 °C. After the mixture was stirred for an additional 2–7 h at 0 °C, the solid was collected by filtration, washed with *n*-pentane, and dried under high vacuum to afford the crude tosylhydrazone. Material at this level of purity was used immediately in subsequent cyclizations to the azoalkanes. These aldehyde tosylhydrazones could be purified further, but only at the expense of substantial amounts of material. Thus, a single recrystallization

of 5-methyl-5-hexenal tosylhydrazone (**2b**) from EtOH was accompanied by nitrogen evolution and led to the recovery of only 38% of the hydrazone. Nevertheless, multiple (two to seven) recrystallizations from *n*-pentane–ether were employed to obtain material for the following spectroscopic data.

5-Methyl-5-hexenal tosylhydrazone (2b): 94% crude yield; mp 53.5–54.5 °C dec; IR (KBr) 3190, 1634, 1592, 1360, 1170 cm^{-1}; NMR (δ, $CDCl_3$) 1.62 (3 H, bs), 1.1–2.3 (6 H, m) 2.38 (3 H, s), 4.45–4.65 (2 H, bm), 7.0–8.0 ppm (6 H, m).

5-Hexenal tosylhydrazone (2c): 74% crude yield; mp 57–58 °C dec; IR (KBr) 3185, 1635, 1593, 1357, 1167 cm^{-1}; NMR (δ, $CDCl_3$) 1.1–2.4 (6 H, m), 2.40 (3 H, s), 4.8 and 5.0 (2 H, m), 5.3–6.1 (1 H, m), 7.0–8.0 ppm (6 H, m).

4-Methyl-4-pentenal tosylhydrazone (2e): 98% crude yield; mp 69–70 °C dec; IR ($CHCl_3$) 3205, 1648, 1596, 1360, 1162 cm^{-1}; NMR (δ, $CDCl_3$) 1.63 (3 H, s), 2.0–2.4 (4 H, m), 2.42 (3 H, s), 4.60 (2 H, bs), 7.0–7.9 ppm (6 H, m).

4-Pentenal tosylhydrazone (2f): 98% crude yield; mp 64–65.5 °C dec; IR (KBr) 3180, 1635, 1590, 1350, 1160 cm^{-1}; NMR (δ, $CDCl_3$) 2.05–2.35 (4 H, bm), 2.42 (3 H, s), 4.7–6.0 (3 H, vinyl pattern), 7.30 and 7.81 (4 H, AA′BB′, J = 8 Hz), 7.3 ppm (1 H, b).

Preparation of 1,5-Dimethyl-6,7-diazabicyclo[3.2.1]oct-6-ene (1a). To a solution of 3.126 g (10.6 mmol) of 6-methyl-6-hepten-2-one tosylhydrazone (**2a**) in 100 mL of anhydrous CH_2Cl_2 was added with stirring at 0 °C 1.84 g (13 mmol) of $BF_3{\cdot}Et_2O$. The reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h. The reaction mixture was concentrated by removing solvent through a distillation column. The yellow residue was dissolved in 40 mL of ether and the ethereal solution extracted with 1 M K_2CO_3 (3 × 10 mL). The combined aqueous washings were extracted further with ether (2 × 10 mL) and the combined ethereal extracts dried by filtration through $MgSO_4$. The solvent was removed by distillation through a column and the azoalkane obtained from the residue by a trap-to-trap distillation (0.025 mm). A second Kugelrohr distillation (130–140 °C, 1 atm) afforded the pure (99% by GLC) azoalkane **1a**: 1.273 g (9.22 mmol, 87%); IR (neat) 1520 cm^{-1}; NMR (δ, $CDCl_3$) 0.9–1.7 (8 H, m), 1.60 ppm (6 H, s); UV (*n*-pentane) 351 nm (ϵ 192). Anal. ($C_8H_{14}N_2$) C, H, N.

Preparation of 1-Methyl-6,7-diazabicyclo[3.2.1]oct-6-ene (1b). To a solution of 2.162 g (7.72 mmol) of 5-methyl-5-hexenal tosylhydrazone (**2b**), in 50 mL of anhydrous CH_2Cl_2 at 0 °C was added with stirring 1.28 g (9.0 mmol) of $BF_3{\cdot}Et_2O$. After 0.5 h the azoalkane **1b** was isolated in the manner described in the previous procedure to afford 0.337 g (2.72 mmol, 35%). The yield of this step could be improved to 46% by starting with recrystallized tosylhydrazone, but the losses incurred in purifying the tosylhydrazone more than compensated for this improvement. An analytical sample of **1b** had IR (neat) 1530 cm^{-1}; NMR (δ, $CDCl_3$) 0.9–2.0 (8 H, m), 1.62 (3 H, s), 4.96 ppm (1 H, bt, J = 5 Hz); UV (*n*-pentane) 349 nm (ϵ 140). Anal. ($C_7H_{12}N_2$) C, H, N.

Preparation of 6,7-Diazabicyclo[3.2.1]oct-6-ene (1c). To a solution of 1.691 g (6.36 mmol) of 5-hexenal tosylhydrazone (**2c**) in 60 mL of anhydrous CH_2Cl_2 at 0 °C was added with stirring 1.13 g (8.0 mmol) of $BF_3{\cdot}Et_2O$. After 4 h at 0 °C and 20 h at room temperature the azoalkane **1c** was isolated in the manner described above to afford 0.100 g (0.909 mmol, 14%) of the crude crystalline substance. The compound was purified by two sublimations: mp ca. 140 °C;[24] IR ($CHCl_3$) 1510 cm^{-1}; NMR (δ, $CFCl_3$) 0.7–1.9 (8 H, m), 4.81 ppm (2 H, bt, J = 5 Hz); UV (*n*-pentane) 347 nm (ϵ 305). Anal. ($C_6H_{10}N_2$) C, H, N.

Preparation of 1,4-Dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1d) and 5,8,8-Trimethyl-3-(3′-methyl-3′-butenyl)-1,2-diazabicyclo-[3.3.0]oct-2-ene (7). A solution of 0.500 g (1.78 mmol) of 5-methyl-5-hexenone tosylhydrazone (**2d**) and 0.33 g (2.3 mmol) of $BF_3{\cdot}Et_2O$ in 50 mL of benzene was refluxed for 6 h. The reaction was quenched by the addition of 30 mL of 1 M K_2CO_3. The benzene solution was washed with saturated NaCl (2 × 15 mL), dried, and concentrated by removal of solvent through a distillation column. The azoalkane **1d** was isolated from this residue by a trap-to-trap distillation (0.03 mm) followed by a Kugelrohr distillation (110–120 °C, 1 atm) to afford 0.094 g (0.76 mmol, 43%). An analytical sample was obtained by column chromatography on silica gel followed by molecular distillation: IR (neat) 1503 cm^{-1}; NMR (δ, $CDCl_3$) 0.8–1.7 (6 H, m), 1.82 ppm (6 H, s); UV (*n*-pentane) 347 nm (ϵ 174). Anal. ($C_7H_{12}N_2$) C, H, N.

The hydrazone **7** was isolated from the dark, oily residue of the aforementioned trap-to-trap distillation. Column chromatography of this residue (20 g of silica gel, $CHCl_3$) afforded 0.078 g (0.35 mmol, 39%) of hydrazone **7**. Kugelrohr distillation (125–135 °C, 0.05 mm) provided an analytical sample as a pale yellow oil: IR (neat) 3065, 1644 cm^{-1}; NMR (δ, $CDCl_3$, 300 MHz) 1.16 (3 H, s), 1.32 (6 H, s) [$CDCl_3$–C_6D_6 (1:1) resolves to 1.18 (3 H, s) and 1.25 (3 H, s)], 1.77 (3 H, bs), 1.50–1.90 (4 H, complex), 2.25 (2 H, dd, J = 8 and 7 Hz), 2.43 (2 H, dt, J = 7 and 5 Hz), 2.47 (1 H, d, J = 17 Hz), 2.69 (1 H, d, J = 17 Hz), 4.72 ppm (2 H, bs); MS *m/e* 220 (M^+), 205 (100, $M^+ - CH_3$). Anal. ($C_{14}H_{24}N_2$) C, H, N.

Preparation of 1-Methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1e). To a refluxing solution of 0.500 g (3.5 mmol) of $BF_3{\cdot}Et_2O$ in 50 mL of anhydrous CH_2Cl_2 was added over 5.5 h by means of a cold syringe pump 0.700 g (2.63 mmol) of 4-methyl-4-pentenal tosylhydrazone (**2e**) in 12 mL of CH_2Cl_2. The reaction was continued for 18 h at reflux before the azoalkane **1e** was isolated in the manner described in the previous procedure to afford 0.158 g (1.44 mmol, 55%) after Kugelrohr distillation (110–120 °C, 1 atm). An analytical sample was obtained by VPC (80 °C, 10 ft × 1/4 in. Teflon-coated aluminum column packed with 15% SE-30 on Chromosorb P): IR (neat) 1495 cm^{-1}; NMR (δ, $CFCl_3$) 0.75–1.70 (6 H, m), 1.79 (3 H, s), 4.77 ppm (1 H, bs); UV (*n*-pentane) 344 nm (ϵ 155). Anal. ($C_6H_{10}N_2$) C, H, N.

Preparation of 3-(2′-Propenyl)-4-(3′-butenyl)pyrazole (8) and 2-(2′-Propenyl)-8-toluenesulfonyl-7,8-diazatricyclo[4.2.1.0^{3,7}]nonane (9). A solution of 0.766 g (3.04 mmol) of freshly prepared 4-pentenal tosylhydrazone (**2f**) and 0.57 g (4.0 mmol) of $BF_3{\cdot}Et_2O$ in 50 mL of anhydrous CH_2Cl_2 was stirred at room temperature for 17.5 h. The solvent was evaporated and 50 mL of Et_2O was added. The ethereal solution was washed with 5% aqueous $NaHCO_3$ (2 × 25 mL) and dried ($MgSO_4$), and the solvent was evaporated to afford a viscous, yellow oil. Column chromatography on 25 g of silica gel ($CHCl_3$) gave three products. The less polar product **9** (0.185 g, 38%) was recrystallized from methanol (three times) to provide an analytical sample: mp 107–108 °C; IR ($CHCl_3$) 1323, 1163 cm^{-1}; NMR (δ, $CDCl_3$, 300 MHz) 1.07 (1 H, dd, J = 12 and 2.5 Hz), 1.28 (1 H, ddd, J = 3,7, and 7 Hz), 1.60 (1 H, ddd, J = 4.5, 11.5, and 11.5 Hz), 1.79 (1 H, ddd, J = 5.0, 11.5, and 11.5 Hz), 1.94 (1 H, ddd, J = 6.5, 5.0, and 11.5 Hz), 2.11 (2 H, complex, J = 7.5 and 4 Hz), 2.29 (2 H, complex, J = 12, 12, 5, and 7 Hz), 2.43 (3 H, s), 3.06 (1 H, dd, J = 3.0 and 6.5 Hz), 3.73 (1 H, ddd, J = 2.5, 7.5, and 12 Hz), 4.29 (1 H, d, J = 5 Hz), 5.04 (2 H, complex), 5.74 (1 H, complex), 7.31 (2 H, d, J = 6 Hz), 7.88 ppm (2 H, d, J = 6 Hz); MS *m/e* 318 (M^+), 163 (100, $M^+ - Ts$), 91 (100, $C_7H_7^+$). Anal. ($C_{17}H_{22}N_2O_2S$) C, H, N.

The more polar product was a slightly unstable yellow oil **8** (0.088 g, 36%): IR (neat) 3600–2500 (broad), 1647 cm^{-1}; NMR (δ, $CDCl_3$) 2.1–2.9 (4 H, m), 3.16 (2 H, bd, J = 6 Hz), 4.75–5.25 (4 H, m), 5.5–6.3 (2 H, m), 7.27 (1 H, s), 10.18 ppm (1 H, bs); UV (EtOH) 222 nm (log ϵ 3.65); MS *m/e* 162 (M^+), 121 (100, $M^+ - CH_2CH{=}CH_2$).

Along with these two products the chromatography also yielded tosylhydrazine (0.26 g, 43%), which was identified by comparison with authentic material on TLC and by mixture melting point.

X-ray Characterization of 2-(2′-Propenyl)-8-toluenesulfonyl-7,8-diazatricyclo[4.2.1.0^{3,7}]nonane (9). A colorless crystal of $C_{17}H_{22}N_2O_2S$ (**9**) with approximate dimensions 0.25 × 0.50 × 0.85 mm was mounted on a glass fiber with the long axis approximately coincident with the fiber axis and precession photographs of the *hk*0, *hk*1. 0*kl*, 1*kl* layers were taken using Cu Kα radiation. Systematic absences were *h*00, $h = 2n + 1$; 0*k*0, $k = 2n + 1$; 00*l*, $l = 2n + 1$, which are consistent with the unique orthorhombic space group $P2_12_12_1$.[25] The crystal was then transferred to a Syntex diffractometer and optically centered. Least-squares refinement of 15 pairs of reflections with 2θ values in the range $\pm(19–26°)$ gave cell constants a = 7.652 (2), b = 8.311 (2), c = 25.486 (9) Å. Partial oscillation photographs (±14°) were taken about each of the crystal axes to check crystal quality and the correctness of indexing. For four formula units per unit cell the calculated density is 1.30 g cm^{-3} and the measured density is 1.30 (2) g cm^{-3} (neutral buoyancy in cyclohexane–carbon tetrachloride). All measurements were made at room temperature. Intensities were measured as previously described[26] for the 2651 unique reflections with $2\theta \leq 59°$ in the form *hkl*. Mo Kα radiation (λ 0.710 69 Å, graphite monochromator) was used for the $\theta/2\theta$ scans. 2θ ranged from 1° below the calculated position of the Kα_1 peak to 1° above the Kα_2 peak. Scan rates varied from 1 to 4°/min depending on the intensity of the reflection. Four standard reflections were used to check stability and to account for long-term drift. The drift cor-

rection varied from 0.986 to 1.027. Owing to the low absorption coefficient (1.97 cm^{-1}) no absorption correction was applied. Of the 2651 unique normalized structure factors, 2138 had $F_o^2 \geq 2\sigma(F_o^2)$, where a value of 0.03 was used for p, the ignorance factor[27] in calculating $\sigma(F_o^2)$.

The position of the sulfur atom was assigned from a sharpened origin-removed Patterson map. Positions of the remaining nonhydrogen atoms were obtained from electron density syntheses based on phases derived from atoms in known positions. On convergence of refinement with anisotropic thermal parameters, the proper choice of enantiomers was tested by changing all coordinates to their negatives and refining this model to convergence. Both models converged to $R_1 = 0.0903$.[27] Refinement of the original model was continued with inclusion of hydrogen atoms in fixed idealized positions (see Table E[17]) and converged to $R_1 = 0.063$ and $R_2 = 0.058$. In the final cycle of refinement, the average shift per error was 0.008. At this point the choice of enantiomer was again checked and again the models were found to be indistinguishable based on the R values.

A total of 2138 reflections were used to refine 199 variables. A final difference map was essentially featureless. The highest peak (0.5 e A^{-3}) was 0.9 Å from the sulfur atom. Examination of groups of reflections ordered on $\sin\theta/\lambda$ or $|F_o|$ revealed no significant trends in disagreement with the model. Zerovalent scattering curves from Cromer[28] were used for S, O, N, and C. Those for hydrogen were taken from Stewart.[29] Corrections for anomalous dispersion due to S, O, N, and C were made.[30] The final values of $|F_o|$ and F_c are listed in Table F.[17]

Acknowledgment. The authors wish to thank the NSF for financial support (Grant CHE 76-15343) and to express their appreciation to Dr. B. Arison of Merck Sharp and Dohme for his help in the acquisition of 300-MHz NMR data for compounds **7** and **9**.

Supplementary Material Available: Tables A-F, containing atomic positions, bond lengths, angles, root mean square displacements of anisotropic thermal ellipsoids, anisotropic thermal parameters, hydrogen fractional atomic coordinates, and observed and calculated structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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Mechanism of the Reactions of Dimethylsilylene with Oxetanes

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Abstract: Dimethylsilylene reacts with oxetane to give high yields of allyloxydimethylsilane and 2,2-dimethyl-1-oxa-2-silacyclopentane. These products result from decomposition of an initial 1,2-zwitterionic intermediate which is formed by coordination of the electrophilic dimethylsilylene with the oxygen of oxetane. Similar results have been obtained from the reactions of dimethylsilylene with 2-methyloxetane, 2,2-dimethyloxetane, 3,3-dimethyloxetane, and 2-vinyloxetane.

We should like to report a novel insertion reaction of dimethylsilylene into the strained carbon–oxygen single bonds of oxetanes.[1] For example, dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane[2] in oxetane solvent at 0 °C yields allyloxydimethylsilane[3] (I, 38%) and 2,2-dimethyl-1-oxa-2-silacyclopentane[4] (II, 41%). The yields reported are based on the generation of two dimethylsilylenes from each dodecamethylcyclohexasilane.[2] It should be noted that in control experiments no reaction of dimethylsilylene with unstrained aliphatic ethers such as tetrahydrofuran or diethyl

0002-7863/80/1502-1641$01.00/0