shown by the rotational barriers of Table I is, as expected, that of increasingly higher energy as successive NH_2 groups are twisted to a position standing orthogonally to the molecular plane. Hence twisting one NH_2 requires 14.73 kcal mol^{-1}, twisting two NH_2 requires 45.34 kcal mol^{-1}, and twisting three NH_2 requires 111.63 kcal mol^{-1}. The qualitative features of this trend also show up in each of the other calculations which have been cited. The behavior of these rotational barriers is related to the presence of "Y aromaticity" in the molecule. In the planar configuration, that of lowest energy, each of the equivalent CN bonds has double bond character due to the delocalized orbitals associated with the carbon and nitrogen atoms. The first barriers must in a general way be a measure of the energy required to break the π bonding in the CN group about which the rotation is made. At the same time, the remaining CN bonds not involved in rotation become more strongly π bonded than before. This is consistent with the observed shortening of such CN bonds. Hence a second rotation must be energetically more costly than a first rotation because it involves twisting about a π bond whose strength has been enhanced as a reaction to the first twisting. Similarly, Table I shows that twisting about any two CN bonds has the effect of lengthening these bonds but shortening the remaining CN bond even further than before. This shortening reflects a further increase in bond stability, and hence this must correspond to an even higher rotational barrier when a third NH_2 group is twisted. It is as though twisting successive NH_2 groups corresponded to winding increasingly tighter springs.

One may also notice that the barriers described introduce hysterisis effects so that the energy trajectory of one rotation is not a unique function of rotation angle alone but is affected by the history of twistings inflicted at other barriers as well.

In Table I we list a population analysis of the electronic charge density for the guanidinium molecule. The numbers shown are net excess charges associated with the various atomic centers. The analysis is shown for the planar ground state of the molecule and for each of its rotated geometries. The charge distribution tends to be somewhat sensitive to scale factor optimization which has not yet been carried out. Therefore we only point to large trends not expected to change qualitatively with later scale factor optimization. Most importantly we see an alternation of charge sign moving outward from the molecular center at the carbon (highly positive) to nitrogens (highly negative) and to hydrogens (highly positive). This efficient distribution of the ion's net positive charge over atomic centers is consistent with the delocalization of the molecule and is conducive to its electrostatic stability. Moreover, this distribution of charge must be important to the ion's ability to enter into hydrogen bonds and to affect the structure of water. As a first approximation, one may suppose that the magnitude of positive charge carried by the hydrogen atoms will be a measure of the efficacy of formation of hydrogen bonds. Table I shows that the hydrogen atoms are very positive with at least +0.435 electron units of charge for the planar ground state. For comparison, we calculated the excess positive charge on hydrogen in a free water molecule, using the same basis as that used for the results listed in Table I. Thus hydrogen on a free water molecule carried +0.394 electron units of charge. Hence the much more positive hydrogens on guanidinium may be expected on energetic grounds to compete favorably with water molecules for hydrogen bonds to water molecules. In this respect, the charge distributions calculated are consistent with the notion that the guanidinium ion is a structure breaker in solution with water.

Acknowledgment. We thank Professor Santoro for bringing the problems of the electronic structure of the guanidinium ion to our attention and for providing us with a copy of his manuscript on rotational barriers in substituted guanidinium ions in advance of publication. It is a pleasure to acknowledge many interesting discussions with him about this molecule. It is also a pleasure to acknowledge discussions with Professor Barrett. We thank Barbara Rubensohn for constructing Figure 1.

Registry No. Guanidinium ion, 43531-41-5.

Synthetic Applications of *N*-Sulfonylamines. 2. Novel Reactions with Ynamines To Form Heterocycles[1]

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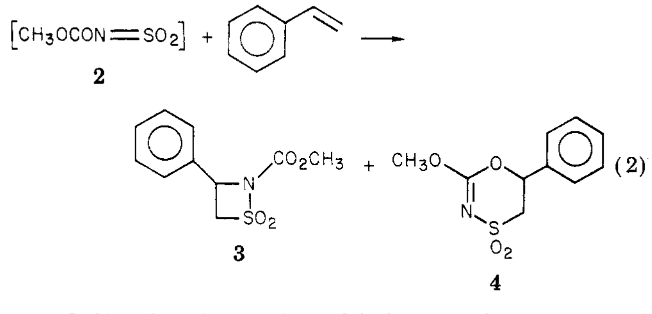
N-Sulfonylamines (**2**) are a class of heterocumulene first characterized by Burgess.[2] While they are not stable to isolation, they are readily generated in situ from the corresponding sulfamoyl chloride (**1**) via dehydrohalogenation (eq 1). These heterocumulenes are reactive electrophiles,

$$\underset{\mathbf{1}}{RNHSO_2Cl} \xrightarrow{-HCl} \underset{\mathbf{2}}{[RN{=}SO_2]} \qquad (1)$$

and Burgess isolated products from their addition reactions with various nucleophiles and olefins.[3]

Of particular interest were the reactions of *N*-sulfonylurethane **2** ($R = CO_2CH_3$).[4] This heterocumulene was relatively stable in solution and offered the advantage of being capable of cycloaddition-like reactions in both a 2 + 2 and a 4 + 2 sense. For example, reaction of **2** ($R = CO_2CH_3$) with styrene gave mixtures of the 2-(carbomethoxy)-1,2-thiazetidine **3** and the 5,6-dihydro-2-methoxy-1,4,3-oxathiazine **4** shown in eq 2.[4]



N-Sulfonylurethane **2** ($R = CO_2CH_3$) has been generated by two methods. The first is simple dehydrohalogenation of the corresponding sulfamoyl chloride (eq 1) using sodium hydride.[4] The second involves in situ fragmentation

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[1] For Part 1, see J. A. Kloek and K. L. Leschinsky, *J. Org. Chem.*, 44, 305 (1979).

[2] G. M. Atkins, Jr., and E. M. Burgess, *J. Am. Chem. Soc.*, **89**, 2502 (1967).

[3] G. M. Atkins, Jr., and E. M. Burgess, *J. Am. Chem. Soc.*, **94**, 6135 (1972).

[4] E. M. Burgess and W. M. Williams, *J. Am. Chem. Soc.*, **94**, 4386 (1972).

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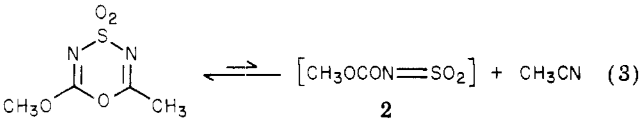
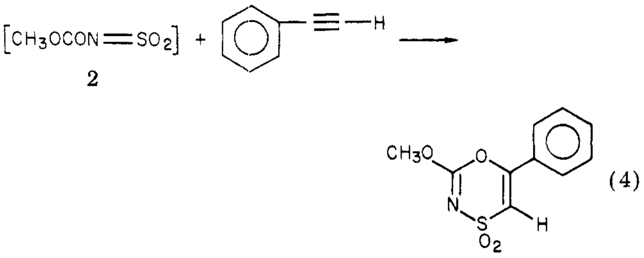
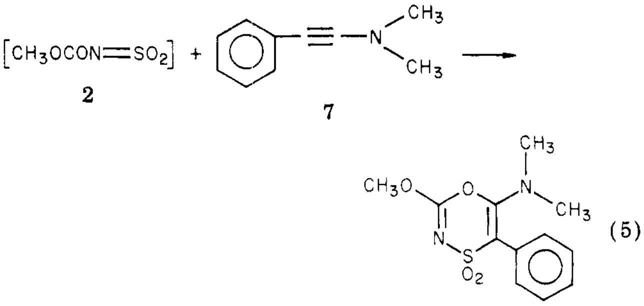
of 1,4,3,5-oxathiadiazine dioxide 5 into 2 and acetonitrile (eq 3).[5] This fragmentation is apparently thermodynamically controlled, with the equilibrium favoring the cyclized material 5. Because only small amounts of 2 are in solution at any given point, reactions at higher temperatures and for longer times are possible.


5 2 (3)

We desired to prepare a number of 1,4,3-oxathiazine 4,4-dioxides, and we were therefore intrigued by Burgess' report that 2 reacted with phenylacetylene to provide 1,4,3-oxathiazine 6 (eq 4).[4] We have successfully employed this useful reaction with a variety of acetylenic substrates and found it to be of general synthetic utility.

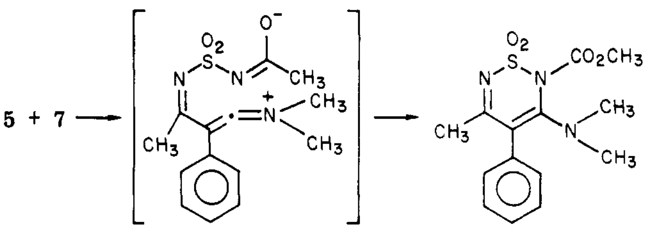

2 6 (4)

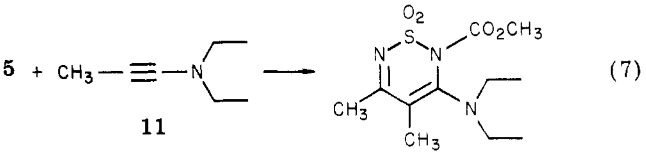
However, when reactions between *N*-sulfonylurethane 2 as well as its precursor 5 and various ynamines were examined, interesting and unexpected results were obtained. Low-temperature generation of 2 using the sodium hydride method (eq 1)[4] followed by treatment with ynamine 7[6] gave rise to the expected oxathiazine 8 (eq 5).


2 7 8 (5)

The structure of this heterocycle was assigned from spectral and elemental analysis as well as analogy to Burgess' work.[4] Particularly noteworthy was the ^{1}H NMR spectrum which consisted of three singlets.

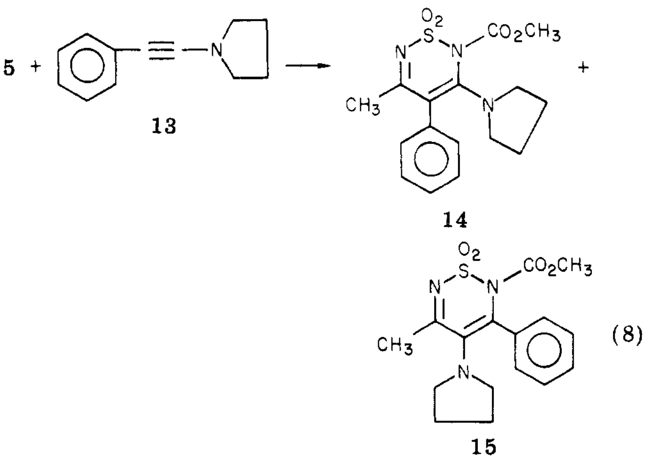
An attempt to reprepare 8 by using the more convenient oxathiadiazine 5[5] to generate 2 provided a totally different product which analyzed for $C_{14}H_{17}N_3O_4S$. Its ^{1}H NMR spectrum displayed a fourth singlet at δ 2.06, and its IR spectrum showed an ester carbonyl absorption. On this basis, as well as ^{13}C NMR data to be presented below, this product was assigned as 1,2,6-thiadiazine dioxide 9 (eq 6). This is the first example of oxathiadiazine dioxide 5 reacting as a discrete entity and retaining the elements of acetonitrile. No trace of 8 was observed. This reaction is general; for example, 5 and ynamine 11 gave rise to 12 (eq 7).

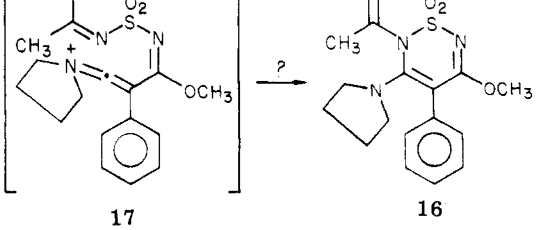

10 9 (6)


11 12 (7)

Mechanistically, the formation of these products can be rationalized by invoking the intermediacy of a ring-opened species such as 10, which recyclizes to give products such as 9 and 12. Such an intermediate could arise either by nucleophilic attack by the ynamine at C-6 of 5 (which would result in direct ring opening) or by cycloaddition of the ynamine across the N-5/C-6 double bond to give a bicyclic intermediate which then could fragment to give rise to 10.[8]

A further surprise manifested itself when the reaction between 5 and ynamine 13[6] afforded two products, a major isomer 14 and a minor isomer 15 (eq 8). These structures were assigned on the following basis. Both compounds analyzed for $C_{16}H_{19}N_3O_4S$, and their ^{1}H NMR spectra were nearly identical (see Experimental Section). Since these compounds were clearly isomeric, our initial speculation was that the major isomer was 14, arising in a fashion similar to 9 (vide supra). It was therefore reasonable to expect that the minor isomer would be 16, which would arise from an intermediate (17) similar to 10.


13 14 15 (8)


17 16

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[5] E. M. Burgess and W. M. Williams, *J. Org. Chem.*, **38**, 1249 (1973).

[6] H. G. Viehe, Ed., "The Chemistry of Acetylenes", Marcel Dekker, New York, 1969, and references cited therein.

[7] Purchased from Fluka Chemical Co.

[8] We are indebted to a referee for this latter suggestion.

However, doubt was cast on this assignment of the minor isomer as **16** by its infrared spectrum which showed an ester absorption nearly identical with that shown by major isomer **14**. That the minor isomer was in fact **15** rather than **16** was confirmed by the ^{13}C NMR spectra of both **14** and **15**. The fully decoupled spectrum of **14** had three peaks of particular interest at 55.5, 151.7, and 177.7 ppm. In an off-resonance-decoupling experiment the resonance at 55.5 ppm became a quartet, while the other two remained singlets. The singlet at 151.7 ppm and the quartet at 55.5 ppm can therefore be respectively assigned as the carbonyl and methoxy carbons of the ester in **14**, while the singlet at 177.7 ppm must be the olefinic ring carbon bearing two nitrogens. The fully decoupled spectrum of the minor isomer showed absorptions at 58.8 and 151.7 ppm and no resonance below 162 ppm. Off-resonance decoupling revealed the signal at 55.8 ppm to be a quartet and the singlet at 151.7 ppm to be unchanged. Therefore, both products have nearly identical ester groups. In addition, if the minor product were **16**, an acetamide carbonyl at 168–173 ppm[9] as well as an olefinic ring carbon bearing two nitrogens at ~177 ppm (vide supra) would be expected. Neither are present. The minor isomer must therefore be **15**.

A number of other ynamines were examined as substrates for this reaction, and only those derived from cyclic amines gave rise to this minor isomer. Since ynamines are, in principle, ambident nucleophiles, it is tempting to speculate that formation of this minor isomer proceeds via an intermediate derived from initial nucleophilic attack on **5** by nitrogen, rather than carbon.

In summary, the reactions between ynamines and *N*-sulfonylurethanes and their precursors are quite versatile in terms of their potential for heterocyclic synthesis. Condensation of directly generated *N*-sulfonylurethane **2** with ynamines gives rise to a family of 1,4,3-oxathiazine dioxides such as **6**. On the other hand, condensation with *N*-sulfonylurethane precursor **5** provides a new and effective route to certain highly functionalized 1,2,6-thiadiazine dioxides. This latter reaction is the first example of 1,4,3,5-oxathiadiazine dioxide **5** reacting prior to fragmentation (eq 3) and as such represents a significant extension of the synthetic utility of *N*-sulfonylamines and their precursors.

Experimental Section

General Methods. Melting points were determined on a Laboratory Devices Melt-temp apparatus and are uncorrected. Nuclear magnetic resonance spectra (NMR) were recorded on Varian T-60 and EM-360 and JEOLCO FX 100 spectrometers using tetramethylsilane as an internal standard. Combustion analyses were performed by Atlantic Microlabs. Dry-column chromatography was accomplished on ICN activity 111/30 silica gel, and elution was done with distilled solvents. Evaporative bulb-to-bulb distillations were performed with a Buchi Kugelrohr hot-air oven. The boiling points reported for this technique are therefore the oven temperature at which distillation occurred. The drying process referred to in the workup procedure involved swirling the solution over an excess amount of anhydrous magnesium sulfate, followed by filtration. Anhydrous THF was obtained by distillation from sodium metal (benzophenone indicator) and stored under argon in a Schlenk flask. Anhydrous acetonitrile was distilled from P_2O_5 and similarly stored. The yields reported are of analytically pure material. No attempt has been made to maximize them.

6-(Dimethylamino)-2-methoxy-5-phenyl-1,4,3-oxathiazine 4,4-Dioxide (8). A slurry of 0.55 g (11.5 mmol) of 50% sodium hydride dispersion (washed with hexane to remove the mineral oil) in 10 mL of anhydrous THF was stirred under a nitrogen atmosphere and cooled in a dry ice/acetone bath. A solution of 2 g (11.5 mmol) of sulfamoyl chloride **1** ($R = CO_2CH_3$) in 10 mL of anhydrous THF was then added dropwise. Stirring was continued an additional 0.25 h, and the solution was brought to −25 °C. A solution of 1.67 g (11.5 mmol) of ynamine **7** in 10 mL of anhydrous THF was added dropwise. Stirring was continued at that temperature for 1 h and at 25 °C for 1 h, whereupon the solution was filtered and concentrated. The resulting oil was taken up in methanol and cooled to −78 °C whereupon 1.3 g (40%) of oxathiazine **8** crystallized. Filtration isolated these crystals: mp 92–94 °C dec; NMR ($CDCl_3$) δ 2.67 (s, 6 H), 4.03 (s, 3 H), 7.43 (s, 5 H).

Anal. Calcd for $C_{12}H_{14}N_2O_4S$: C, 51.05; H, 5.00; N, 9.92. Found: C, 50.82; H, 5.07; N, 9.83.

3-(Dimethylamino)-2-(methoxycarbonyl)-5-methyl-4-phenyl-1,2,6-thiadiazine 1,1-Dioxide (9). A solution of 1.45 g (10 mmol) of ynamine **7** in 10 mL of anhydrous acetonitrile was stirred under N_2 and cooled in a dry ice/acetonitrile bath. A solution of oxathiadiazine **5** in 20 mL of anhydrous acetonitrile was added dropwise, and the resulting solution was stirred for 1 h and then concentrated to a dark, gummy residue. This mixture was chromatographed on a silica gel dry column by using 40% ethyl acetate/cyclohexane as the eluant. Extraction of the appropriate band with ethyl acetate gave 1.7 g of a pale yellow oil which crystallized on standing. Trituration with ether afforded 0.8 g (20%) of thiadiazine **9** as a crystalline solid: mp 117–120 °C; NMR ($CDCl_3$) δ 2.06 (s, 3 H), 2.63 (s, 6 H), 3.93 (s, 3 H), 7.23 (s, 5 H); IR ($CHCl_3$) 1750 cm^{-1}.

Anal. Calcd for $C_{14}H_{17}N_3O_4S$: C, 52.01; H, 5.26; N, 13.00. Found: C, 51.97; H, 5.28; N, 12.97.

3-(Diethylamino)-4,5-dimethyl-2-(methoxycarbonyl)-1,2,6-thiadiazine 1,1-Dioxide (12). A solution of 1.25 g (0.011 mol) of ynamine **11** in 10 mL of anhydrous acetonitrile was stirred under nitrogen and cooled in a dry ice/acetonitrile bath. A solution of 2.0 g (0.011 mol) of oxathiadiazine **5** in 25 mL of anhydrous acetonitrile was then added dropwise. When the addition was complete, the mixture was allowed to come to room temperature and then concentrated to provide 3.4 g of an oil which crystallized on standing. These crystals were extracted into boiling ether, which was hot filtered and allowed to cool. A yellow solid (1 g, 31%) precipitated which proved to be 1,2,6-thiadiazine **12**: mp, 83–86 °C; NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 6 H), 1.90 (s, 3 H), 2.30 (s, 3 H), 3.23 (q, J = 7 Hz, 4 H), 3.93 (s, 3 H); mass spectrum *m/e* 289.

Anal. Calcd for $C_{11}H_{19}N_3O_4S_1$: C, 45.66; H, 6.62; N, 14.52. Found: C, 45.23; H, 6.47; N, 14.44.

2-(Methoxycarbonyl)-5-methyl-4-phenyl-3-pyrrolidino-1,2,6-thiadiazine 1,1-Dioxide (14) and 2-(Methoxycarbonyl)-5-methyl-3-phenyl-4-pyrrolidino-1,2,6-thiadiazine 1,1-Dioxide (15). A solution of 2.0 g (0.011 mol) of oxathiadiazine **5** in 25 mL of anhydrous acetonitrile was stirred under nitrogen and cooled in a dry ice/acetonitrile bath. A solution of 1.93 g (0.011 mol) of ynamine **13** was added dropwise, and the resulting mixture was allowed to come to room temperature. After filtration and concentration, the mixture was chromatographed on 100 g of silica gel by using 40% ethyl acetate/cyclohexane as the eluant. The first material off the column was 0.8 g (20%) of thiadiazine **15**, which crystallized from ether: mp 103–106 °C; ^1H NMR ($CDCl_3$) δ 1.91 (m, 4 H), 3.40 (m, 4 H), 3.95 (s, 3 H), 7.18 (m, 5 H); ^{13}C NMR ($CDCl_3$, fully decoupled) 23.65, 25.83, 49.12, 55.83, 109.30, 127.48, 128.36, 131.24, 134.48, 151.72, 158.30, 162.01 ppm; IR ($CHCl_3$) 1750, 1660, 1560 cm^{-1}.

Anal. Calcd for $C_{16}H_{19}N_3O_4S_1$: C, 55.01; H, 5.44; N, 12.03. Found: C, 54.91; H, 5.48; N, 12.00.

The second material off the column was 1.5 g (38%) of thiadiazine **14** which crystallized from ether: mp 146–148 °C; ^1H NMR ($CDCl_3$) δ 1.83 (m, 4 H), 2.03 (s, 3 H), 3.23 (m, 4 H), 4.03 (s, 3 H), 7.45 (s, 5 H); ^{13}C NMR ($CDCl_3$, fully decoupled) 24.88, 26.06, 51.53, 55.53, 104.30, 128.25, 128.65, 132.54, 136.07, 151.72, 153.01, 177.77 ppm; IR ($CHCl_3$) 1760 (s), 1745, 1575 cm^{-1}.

Anal. Calcd for $C_{16}H_{19}N_3O_4S_1$: C, 55.01; H, 5.44; N, 12.03. Found: C, 54.89; H, 5.49; N, 11.95.

Acknowledgment. We wish to thank Professor Burgess for his helpful discussion during the inception of this

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[9] G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, 1972, p 123.

work and for graciously providing us with detailed experimental results of a portion of his own research.

Registry No. 1 (R = CO_2CH_3), 36914-92-8; 5, 40028-33-9; 7, 4604-65-3; 8, 72207-02-4; 9, 72207-03-5; 11, 4231-35-0; 12, 72207-04-6; 13, 54494-80-3; 14, 72207-05-7; 15, 72207-06-8.

Flow System Pyrolysis of 7,7-Dimethylbicyclo[4.1.1]octa-2,4-diene

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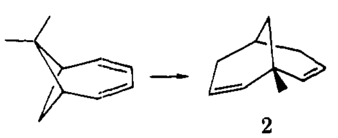
Received July 31, 1979

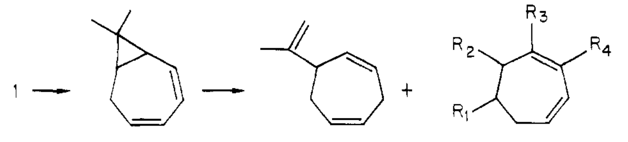
As part of our study of the chemistry of 7,7-dimethylbicyclo[4.1.1]octa-2,4-diene (1),[1] we have investigated its flow system pyrolysis. At temperatures of 350 °C and above we find the thermodynamically favored rearrangement product to be 1-methylbicyclo[3.3.1]nona-2,7-diene (2). We have isolated a number of the compounds formed at lower temperatures and subjected them to repyrolysis. On the basis of the results of these studies, we propose a mechanism for the rather remarkable transformation of 1 to 2.



1 2

Results

When the pyrolysis of 1 is carried out at 250 °C, although about 85% of 1 remains unreacted, the major rearrangement product is (Table I) 8,8-dimethylbicyclo[5.1.0]octa-2,4-diene (3).[2] This product of a 1,5 carbon shift in 1 is the only isomer detected when 1 is irradiated through Pyrex or when the pyrolysis is conducted at 225 °C. When 3 is repyrolyzed at 250 °C, 3–8 are obtained in ratios similar to those measured when 1 is pyrolyzed; however, no 1 is detected. Thus, the equilibrium between 1 and 3 apparently favors the latter diene.



3 4 5, $R_1 = CH_3C{=}CH_2$
6, $R_2 = CH_3C{=}CH_2$
7, $R_3 = CH_3C{=}CH_2$
8, $R_4 = CH_3C{=}CH_2$

Repyrolysis of 4–8 at 250 °C shows that 5–8 are readily interconverted but that they do not equilibrate with 4 at this temperature. These results are consistent with the fact that the 1,5 hydrogen shifts that interconvert 5–8 are allowed by orbital symmetry whereas the 1,3 shifts necessary to transform 4 into any one of the latter four cycloheptadienes are forbidden.[3]

The structures of 7 and 8 rule out both these molecules as the primary product of a sigmatropic rearrangment in either 1 or 3. In order to determine whether 5 or 6 is the first-formed product in the pool of interconvertible cycloheptadienes, 5 and 6 were repyrolyzed at 250 °C so that the compositions of the resulting mixtures of 5–8 could be compared with those obtained by pyrolysis of 1 and 3. Since 5 and 6 are formed as minor products in the pyrolysis of both 1 and 3, it was necessary to synthesize 5 and 6 independently to obtain sufficient quantities for the repyrolysis studies.

Table I. Composition of the Product Mixture Formed from 1 at 250 and 350 °C

	product distribution, %						
temp, °C	2	3	4	5	6	7	8
250[a]		41	24	3	7	19	6
350[b]	4		29			39	28

[a] At this temperature approximately 85% of 1 is recovered. [b] At this temperature several small peaks with relatively short retention times make up about 10% of the total product mixture.

Table II. Composition of the Mixture of 5–8 Formed from 1, 3, 5, and 6 at 250 °C

	product distribution, %			
reactant	5	6	7	8
1	9	20	54	17
3	11	22	52	15
5	44	11	34	11
6	11	19	55	15

A mixture of 5 and 6 was prepared by reaction of isopropenyllithium with tropylium fluoroborate, followed by lithium in ammonia reduction of the resulting 7-isopropenylcycloheptatriene.[4] The mixture of 5 and 6 was separated by preparative GLC, and each compound was pyrolyzed at 250 °C. The results (Table II) show that the mixture of 5–8 obtained from 6 corresponds closely to those mixtures formed from 1 and 3 whereas the composition of the mixture obtained from 5 does not. These data provide strong evidence that 6, rather than 5, is formed first. Further proof comes from the pyrolysis of 3 at 225 °C. Although at this temperature conversion of 3 to rearrangement products is very low, the only two isomers of 3 detected are 4 and 6.

When the temperature of the pyrolysis column is raised to 350 °C, only three of the isopropenylcycloheptadienes—4, 7, and 8—are present. A small amount of a new product (2) is also formed. Pyrolysis of 4–8 at this temperature shows that 2 is not formed from 4 but only from the equilibrating pool of cycloheptadienes (5–8). Raising the column temperature further[5] or recycling the pyrolysate leads to an increase in the amount of 2 present. Since 2 is recovered unchanged from pyrolysis at temperatures up to 450 °C, it appears to be the thermodynamically most stable isomer in the region of the potential surface that is accessible from 1 at temperatures up to 450 °C.

The structure of 2 was deduced from spectral data. The ^1H NMR spectrum shows the presence of a methyl group attached to a quaternary carbon, four protons on doubly bonded carbons, and a methylene group split by one proton with $J = 3$ Hz. The absence of UV absorption shows that

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(1) S. D. Young and W. T. Borden, *Tetrahedron Lett.*, 4019 (1976).

(2) S. W. Staley and N. J. Pearl, *J. Am. Chem. Soc.*, **95**, 2731 (1973). We are indebted to Professor Staley for sending us the spectra of 3 for comparison with those of our pyrolysis product.

(3) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

(4) S. W. Staley and D. W. Reichard, *J. Am. Chem. Soc.*, **91**, 3998 (1969).

(5) At temperatures of 400 °C 1,3 hydrogen shifts begin to occur, as evidenced by the partial conversion of 4 to 7 and 8. In addition, 5- and 6-isopropylidenecyclohepta-1,3-diene are found among the pyrolysis products.

0022-3263/80/1945-0724$01.00/0