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## Reinvestigation of the Thermal Rearrangement of Alkenylidenecyclopropanes

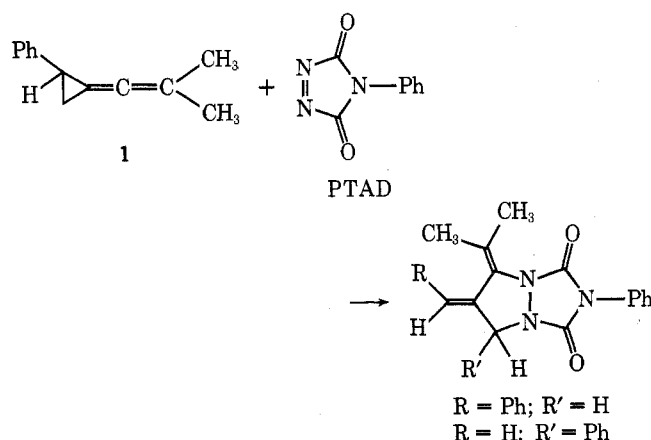
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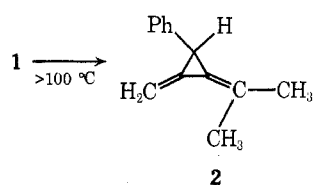
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The thermal rearrangement of alkenylidenecyclopropanes has been reinvestigated. It is concluded that the thermal rearrangements occur via perpendicular trimethylenemethane-type diradicals and that the rearrangement is a typical methylenecyclopropane-type rearrangement. Contrary to the previously reported results, enantiomerization and diastereomerization of alkenylidenecyclopropanes is observed, and the activation enthalpies measured in this study are considerably lower than those reported. Whereas aryl-substituted alkenylidenecyclopropanes undergo thermal rearrangement under the more vigorous conditions required for cycloaddition with less reactive dienophiles, alkyl-substituted alkenylidenecyclopropanes rearrange much more slowly, allowing for reaction with the less reactive dienophiles.

In view of the tremendous synthetic utility of the  $[\pi_4 + \pi_2]$  cycloaddition reaction (i.e., the Diels–Alder reaction) for the construction of variously substituted cyclohexenes and the well-known tendency of the cyclopropyl moiety to mimic the carbon–carbon double bond in certain reactions, we embarked on a program designed to evaluate the synthetic utility of cycloaddition reactions of cyclopropane-containing compounds. Although methylenecyclopropanes<sup>1</sup> and vinylcyclopropanes<sup>2</sup> failed to undergo the desired cycloaddition reactions to form five- and seven-membered ring compounds even with the most reactive of the dienophiles, 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD), alkenylidenecyclopropanes reacted rapidly at 0 °C in the desired manner to form five-membered ring compounds<sup>3</sup> with PTAD.

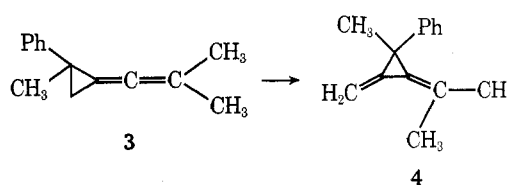


Attempts to react the easily prepared 1 with less reactive dienophiles (maleic anhydride and tetracyanoethylene) at higher temperatures ( $>100$  °C) resulted in the thermal rearrangement of 1 to produce the bisalkylidenecyclopropane 2.<sup>4</sup>



Efforts were temporarily abandoned toward effecting cycloaddition reactions with less reactive dienophiles, and the intimate details of the cycloaddition of alkenylidenecyclopropanes with PTAD were investigated. Theoretical and spectroscopic studies<sup>5</sup> led to an understanding of the nature of the bonding in alkenylidenecyclopropanes and the bonding interactions in the transition state for concerted cycloaddition with PTAD, and the results of a kinetic study gave a value of  $\Delta H^\ddagger$  for the cycloaddition of 1 with PTAD of  $9.6 \pm 1.5$  kcal/mol.<sup>6</sup>

During the early stages of the later investigations the results of a study of the thermal rearrangement of arylsubstituted alkenylidenecyclopropanes were reported.<sup>7</sup> It was reported that the rearrangement of 3 to 4 occurred with a  $\Delta H^\ddagger$  of 30.4



kcal/mol. Intuitively, this value seemed far too high in view of our observation that the rearrangement of 1 proceeded at a reasonable rate at  $\geq 100$  °C. Furthermore, the difference between the  $\Delta H^\ddagger$  of 9.6 kcal/mol for cycloaddition of 1 with PTAD and  $>30.4$  kcal/mol for rearrangement of 1 (the methyl group of 3 should lower the  $\Delta H^\ddagger$  for rearrangement of 3 relative to 1) provides a rather large "thermodynamic window" between which we should have been able to find a dienophile capable of reacting with 1 with a  $\Delta H^\ddagger > 9.6$  but  $<30.4$  kcal/mol. Although the thermal rearrangement of the alkenylidenecyclopropanes appeared to be a typical methylenecyclopropane rearrangement, Sadler and Stewart<sup>7</sup> reported that diastereomerization of substituted alkenylidenecyclopropanes did not occur. In view of these unexpected reported aspects of the thermal rearrangements of alkenylidenecyclopropanes it was decided to reinvestigate the rearrangement reaction.

### Results

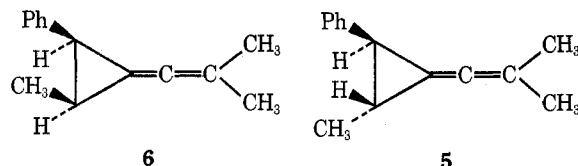
The thermal rearrangements of 1, 3, 5, and 6 were carried out in sealed NMR tubes, the rates of rearrangement being

**Table I. Activation Enthalpies for Rearrangement of Alkenylidenecyclopropanes**

Compd	$\Delta H^\ddagger$ , kcal/mol <sup>a</sup>	Compd	$\Delta H^\ddagger$ , kcal/mol <sup>a</sup>
1	23.0	5	21.5
3	19.6	6	22.6

<sup>a</sup> Values are based on the rates of disappearance of 1, 3, 5, and 6 and do not take into account the contributions from the reverse reaction; however, these contributions are minor.

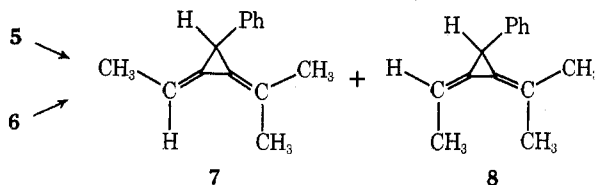
monitored by integration of the periodically recorded NMR spectra. The rates of rearrangement followed excellent first-



order kinetics and varied only slightly over a wide range of solvent polarities. The activation enthalpies for rearrangement in hexadeuteriobenzene were determined and found to be ~10 kcal/mol lower than that reported for 3<sup>7,8</sup> (see Table I).

The composition of the thermolysis products derived from the *cis* and *trans* compounds 6 and 5 was carefully monitored by NMR. During the thermal rearrangement of 6 a doublet appeared at  $\delta$  1.13 (characteristic of the methyl group in 5) which reached a maximum concentration of ~7% and then decreased to zero. Similarly, during the rearrangement of 5, the doublet characteristic of the methyl group in 6 at  $\delta$  0.85 increased to 5.7% and then decreased to zero. *This definitely shows that diastereomerization occurs during the thermal rearrangement of alkenylidenecyclopropanes.*

The thermal rearrangements of 5 and 6 result in the formation of mixtures of the *E* and *Z* isomers 7 and 8, the com-



position of which varies with temperature and starting material (see Table II). The major isomer formed from both 5 and 6 has been assigned structure 8 by Sadler and Stewart<sup>7</sup> based on the observation that the vinyl hydrogen of the minor isomer 7 appears at lower field ( $\delta$  5.83) than in the major isomer ( $\delta$  5.53), which was attributed to long-range deshielding by the adjacent double bond. Inspection of models, however, indicates that the vinyl hydrogen is not in a strongly deshielding region of the C=C. Of apparently greater importance is the fact that the vinyl hydrogen of 8 resides in a long-range shielding region of the aromatic ring still consistent with the assignment of Sadler and Stewart. The <sup>1</sup>H chemical shifts of the vinyl methyl group, however, suggest an opposite assignment of structures. The ethylidene methyl and the "inside" methyl of the isopropylidene group in the major isomer appear at lower field ( $\delta$  2.03 and 1.96, respectively) than in the minor isomer ( $\delta$  1.94 and 1.87, respectively), suggesting that minor isomer is 8 in which the higher field shifts of the methyls arises from a steric compression shift. Similar differences in chemical shifts have been observed with the PTAD adducts of alkenylidenecyclopropanes having the partial structures 9 and 10, the methyls in 9 appearing 0.07–0.12 ppm higher field than in 10.<sup>3</sup> (The higher field position of the ethylidene methyl group in 7 can also be attributed to long-range shielding by the aromatic ring. This explanation, how-

**Table II. Composition of Mixtures of 7 and 8 Formed on Pyrolysis of 5 and 6**

Temp, °C <sup>a</sup>	% 7 from 5	% 7 from 6
89.0	2.0	37
103.5	9.8	26
118.6	11.7	20

<sup>a</sup> The equilibration of 7 and 8 occurs much more slowly than does the rearrangement of 5 and 6 to 7 and 8.

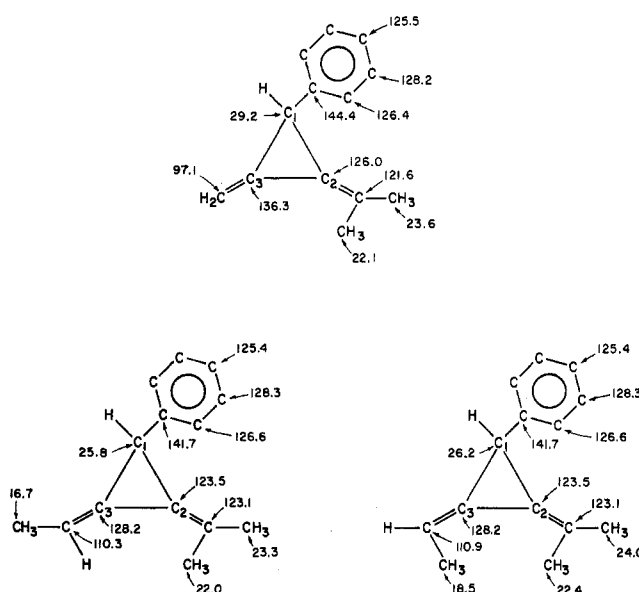
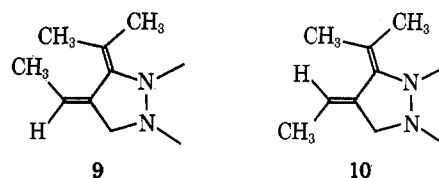


Figure 1. <sup>13</sup>C chemical shifts in 2, 7 and 8.

ever, does not apply to the change in chemical shift of the "inside" methyl of the isopropylidene group.) The <sup>13</sup>C NMR



spectra of the two products show interesting differences (see Figure 1). (Assignment of the resonances to specific carbons is based on an analysis of substituent shift parameters for acyclic dienes.)<sup>9</sup> The <sup>13</sup>C shifts of the ipso aromatic carbon, C<sub>1</sub>, and the ethylidene methyl all appear at higher field in the minor product (a *cis* alkene shift effect),<sup>10</sup> suggesting that the minor product is 7.

On further heating, the mixtures of 7 and 8 undergo slow equilibration to a mixture containing 64% of 7 (at 117 °C), the originally minor isomer formed in the rearrangements of 5 and 6. Careful measurement of the nonbonded distances between the ethylidene methyl carbon and C<sub>1</sub> and the aromatic carbons in 7 reveals that these distances are ~0.05 Å longer than the distances between the ethylidene methyl carbon and C<sub>2</sub> and the carbons of the isopropylidene group, indicating that 7 should be more thermodynamically stable than 8. Finally, analysis of the steric interactions generated during the ring opening and rotational processes (see later discussion on the mechanism of rearrangement) indicate that 8 should be the kinetically favored product from the rearrangement of both 5 and 6. Thus, except for the <sup>1</sup>H chemical shifts of the methyl groups, the data are consistent with the assignment of 8 as the major product formed in the rearrangement of 5 and 6.

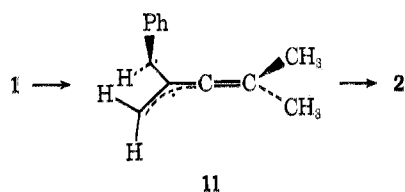
Table III. Rate Constants <sup>a</sup> for the Thermal Rearrangement of 5 and 6

Temp, °C	Cis isomer 6			Trans isomer 5		
	<i>k</i> <sub>total</sub>	<i>k</i> <sub>out</sub>	<i>k</i> <sub>in</sub>	<i>k</i> <sub>total</sub>	<i>k</i> <sub>out</sub>	<i>k</i> <sub>in</sub>
118.6	4.47	3.58	0.89	18.6	16.4	2.18
103.5	1.66	1.23	0.43	4.60	4.15	0.45
89.0	0.40	0.25	0.15	1.37	1.34	0.03

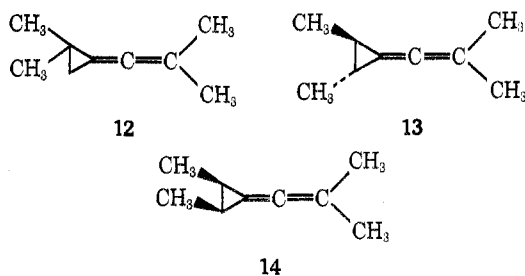
<sup>a</sup> All rate constants  $\times 10^5$  (s<sup>-1</sup>).

### Discussion

Analysis of the thermodynamic data pertaining to the rearrangement of the alkenylidenecyclopropanes indicates that the rearrangement is a typical methylenecyclopropane rearrangement occurring via a perpendicular trimethylenemethane diradical intermediate.<sup>11-14</sup> Subtraction of the methylenecyclopropane strain energy (42)<sup>15</sup> and benzyl radical (-13.5)<sup>16</sup> and allyl radical (-11.6 to -14.0)<sup>17</sup> resonance energies from an average C-C bond dissociation energy (83) plus the resonance energy of the alkenylidenecyclopropane system (3.8 kcal/mol)<sup>5</sup> gives a minimum value for  $\Delta H^\ddagger$  of 17.3-19.7 kcal/mol for the rearrangement of 1 to 2. Thus, the application of Hammond's postulate<sup>18</sup> to the rearrangement of 1 indicates that the transition state for rearrangement must occur very late along the reaction coordinate, and that the transition state structure is nearly that present in the perpendicular trimethylenemethane diradical 11.



Critical to the low enthalpy content of 11 is the benzyl radical portion. If the proposed mechanism of the rearrangement is correct, removal of the phenyl group must result in an elevation of the enthalpy of the diradical and the transition state for its formation by  $\sim 12.4$  kcal/mol. Consistent with this view is the observation that the methylated compounds 12-14 undergo insignificant isomerization at 140 °C



over a period of 24 days. This observation strongly favors a two-step rearrangement over a concerted process in that in a concerted process such a large substituent effect is not anticipated.

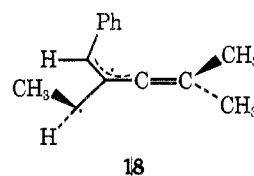
The discrimination in formation of 8 vs. 7 as the major product from both 5 and 6 is determined by steric effects arising in the formation of the diradical intermediates 15 and 16 (see Figure 2). With both 5 and 6 the inward rotation of the methyl group attached to C<sub>2</sub> to form diradical 15 is sterically less favorable than outward rotation to form 16, the inward rotation occurring less rapidly in the cis isomer 6 than in the trans isomer 5 (see partial rates in Table III). It must be noted that there is no adverse steric interaction generated in the outward rotation between the methyl on C<sub>2</sub> and the methyl

of the isopropylidene group of 15 and 16 because of the perpendicular orientation of the isopropylidene group relative to the plane of the trimethylenemethane portion of the diradical. The slightly less favorable steric interaction between the ethylidene methyl and the "inside" methyl of the isopropylidene group is generated on ring closure of 16 in which the isopropylidene group rotates into the plane of the newly formed three-membered ring. Ring closure of 15 and 16 occurs considerably more rapidly than does the interconversion of 15 and 16 via 18, which would involve the sacrifice of the resonance energy of the allyl radical portions of 15 and 16, as is evidenced by the considerably different ratios of 15 and 16 formed from 5 and 6 at the same temperatures and the slow rate of interconversion of 7 and 8.

The slower rate of interconversion of 7 and 8 must be in part due to the greater energy required to cleave a vinyl C-C bond in 7 and 8 relative to the rather weak C<sub>2</sub>-C<sub>3</sub> bond in 5 and 6.<sup>3b</sup> In addition, if the interconversion of 15 and 16 is slow relative to ring closure, the formation of 15 from 7 and 16 from 8 will not result in net interconversion of 7 and 8. Alternatively, both 7 and 8 could open to form diradical 17 in which ring closure to both 7 or 8 is possible. As with 15 and 16, the interconversion of 17 with 15 and 16 again must be slow relative to ring closure.

Although the inward rotation of the methyl group in the cis isomer 6 occurs less rapidly than does the inward rotation in the trans isomer 5 at higher temperatures, the dominant outward rotation of the methyl group occurs more rapidly with the trans than with the cis isomer. This latter result is unexpected in that steric interactions between the phenyl and methyl groups in the cis isomer should result in a higher ground state energy, and hence potentially greater reactivity, than with the trans isomer 5.<sup>19</sup> Unfortunately, a direct comparison of the ground-state energies of 5 and 6 is not possible as at thermal equilibrium at 117 °C the concentrations of 5 and 6 are below the levels of detection (<0.03% of 6 and <0.05% of 5). The greater reactivity of the trans isomer 5 toward thermal rearrangement is in contrast to its lesser reactivity than 6 in cycloaddition with PTAD<sup>6</sup> and reaction with trichloroacetic acid.<sup>20</sup> The reason for the greater reactivity of the trans isomer 5, and the greater discrimination in diradical formation, in thermal rearrangement is not obvious.

The available thermodynamic data allow construction of the qualitatively accurate energy diagram shown in Figure 3. No evidence pertaining to the structure of the transition state for interconversion of 15 and 16, and hence the  $\Delta H^\ddagger$  for the interconversion, is available. Assuming that interconversion of 15 and 16 requires the loss of the allyl radical resonance (via diradical 17),  $\Delta H^\ddagger$  for this process would be  $\geq 11.6$ -14.0 kcal/mol. However, concomitant rotation of the benzyl radical center would form a cinnamyl-type containing diradical (18)



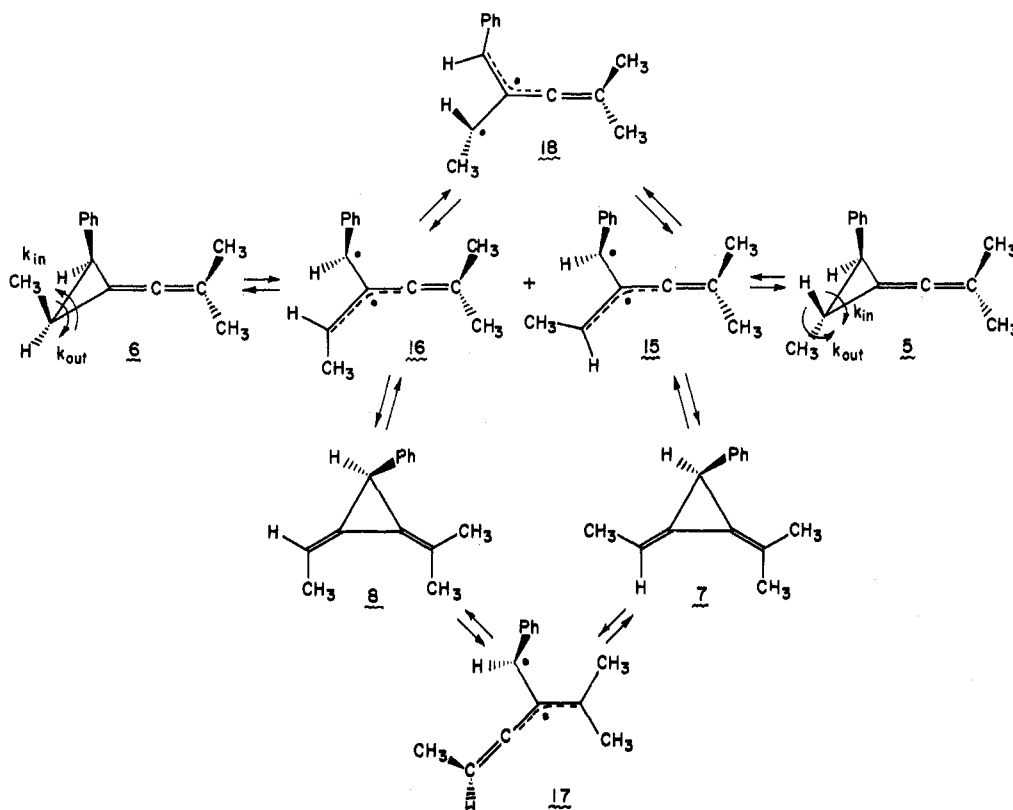


Figure 2. Mechanistic pathway for the thermal rearrangement of 5 and 6 and equilibration of 7 and 8.

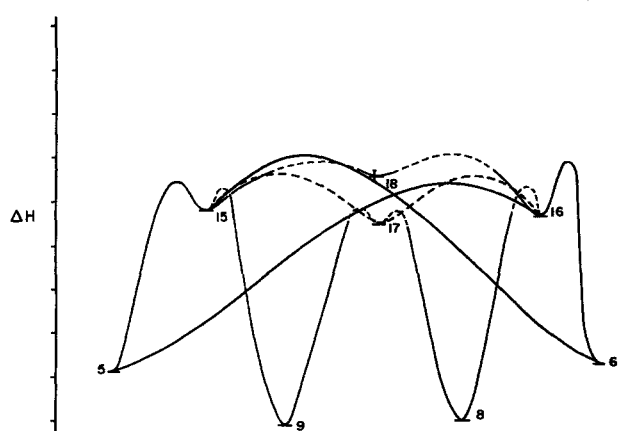


Figure 3. Enthalpy relationships for the thermal rearrangement of 5 and 6 and equilibration of 7 and 8. Each vertical unit represents 5 kcal/mol. Solid lines represent known energy contours, dashed lines represent unknown energy contours.

which should be lower in enthalpy by  $\sim 5$  kcal/mol compared to 17. The energy of diradical 17 should be somewhat lower than either 15 or 16 owing to the additional methyl group attached to the allyl radical portion of 17. Reversion of 18 to the more stable diradical system represented in 15 and 16 can occur to produce either 15 or 16, or their enantiomerically related diradicals, in which case loss of optical purity would occur on reversion to 5 and/or 6. Experiments carried out with optically active **1**<sup>21</sup> indicate that racemization of **1**, and possibly of **2**, does occur at higher temperatures.<sup>22</sup> The optical rotation of a mixture of **1** and **2** formed by partial thermal isomerization of (*R*)-(-)-**1** in benzene at  $\sim 120$  °C indicates that both **1** and **2** are still optically active,<sup>23</sup> but vapor-phase pyrolysis at temperatures above  $\sim 220$  °C produces an optically inactive mixture of **1** and **2**. In view of all of the experimental data, it must be concluded that the thermal rear-

Table IV. First-Order Rate Constants for the Thermal Rearrangement of Alkenylidenecyclopropanes

Temp, °C	$k \times 10^5, \text{s}^{-1} \text{ }^a$			
	1	3	5	6
89.0	0.09	0.39	1.37	0.40
103.5	0.39	1.13	4.60	1.66
117.0	1.11			
118.6		2.90	13.6	4.47
127.0	1.60			
138.0	3.80			

<sup>a</sup> Rate constants for disappearance of starting material at low conversions.

rangements of alkenylidenecyclopropanes occur via a typical methylenecyclopropane rearrangement pathway.

### Experimental Section

#### Thermal Rearrangement of Alkenylidenecyclopropanes.

Samples (100–150 mg) of the alkenylidenecyclopropanes were dissolved in 1.0 ml of hexadeuteriobenzene in NMR tubes. The solutions were triply freeze-degassed and sealed under vacuum. The sample tubes were placed in constant-temperature sand baths, removed periodically, and chilled with ice water, and the NMR spectra recorded and integrated. The data gave excellent first-order kinetic plots. The rate constants are listed in Table IV.

The thermal rearrangement of **1** was also carried out in other solvents at 117 °C as described above giving the rate constants ( $\times 10^6 \text{ s}^{-1}$ ) 1.1 ( $\text{CCl}_4$ ), 1.3 ( $\text{CDCl}_3$ ), 0.9 ( $\text{CH}_3\text{CN}$ ), and 1.0 ( $\text{CD}_3\text{SOCD}_3$ ).

**Thermal Equilibration of 7 and 8.** A solution of 150 mg of a mixture of **7** and **8** (18.7% **7**) in 0.75 ml of hexadeuteriobenzene was placed in an NMR tube, triply freeze-degassed, sealed under vacuum, and was heated in a sand bath at 117 °C. The sample was periodically removed and the NMR spectrum was recorded and integrated. The change in composition of the mixture with time was as follows: time in hours (%**7**) 23.5 (29.8); 109 (34.7); 181 (45.0); 373 (51.4); 469 (57.8); 829 (60.9); 1152 (63.0); 2592 (64.1). No **5** or **6** could be detected at the end of the equilibration process.

Registry No.—1, 4544-23-4; 2, 30896-86-7; 3, 40922-91-6; 5, 33530-27-7; 6, 33530-26-6; 7, 40811-43-6; 8, 40811-42-5.

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- (19) The lesser reactivity of **6** cannot be the result of a greater reactivity in ring closure of **16** to re-form **6**, relative to re-formation of **5** from **15**, because of the greater steric strain in **6**.
- (20) D. J. Pasto, unpublished observations.
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- (23) Attempts to separate **1** and **2** have met with failure and, thus, it has not yet been possible to determine the optical purities of **1** and **2**.

## Bridged Polycyclic Compounds. 84. Cationic Rearrangements Accompanying Addition of Acetic Acid to the Cyclopropane Dibenzotricyclo[3.2.2.0<sup>2,4</sup>]nonadiene<sup>1</sup>

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Acid-catalyzed addition of acetic acid at reflux to 6,8-dibenzotricyclo[3.2.2.0<sup>2,4</sup>]nonadiene (**1**) gives a mixture of *cis*-8-methyl-7-dibenzobicyclo[2.2.2]octadienyl acetate (**5**), the *trans* isomer (**6**), and 6,8-dibenzo-2-bicyclo[3.2.2]nonadienyl acetate (**7**). Low temperature and deuterium-labeling experiments indicate that these products are thermodynamic sinks and that the initial products of addition are undoubtedly *syn*-8-methyl-*exo*-2-dibenzobicyclo[3.2.1]octadienyl acetate (**8**) and 3,6-dibenzo-2-bicyclo[3.2.2]nonadienyl acetate (**24**). The paths which are traversed in the acid-catalyzed rearrangements are explored, and rough rates of isomer interconversions are reported. The experimental results are discussed, with special attention paid to the differences between the isomeric [3.2.2] system and its demethylene analogue, the dibenzobicyclo[2.2.2]- and [3.2.1]octadienyl system.

Our interest in the stereochemistries and mechanisms of electrophilic additions to cyclopropanes<sup>2</sup> led us to a study of additions to 6,8-dibenzotricyclo[3.2.2.0<sup>2,4</sup>]nonadiene (**1**). This cyclopropane offers a variety of paths for ring-opening additions, and, as will be seen below, avails itself of several of these.

Several methods were attempted for the synthesis of **1**. Of these, the Gindig-Cross modification<sup>3</sup> of the Simmons-Smith reaction<sup>4</sup> with **2** gave **1** in about 70% yield. As the synthesis of **2** requires several steps, the following alternative synthesis was somewhat more convenient. Anthracene was condensed with *cis*- or *trans*-1,3-dichloropropene to give **3** or **4**, respectively. Treatment of either isomer with heavily coppered zinc-copper couple (1 g-atom of copper to 6 of zinc) gave **1** in good yield.<sup>5</sup>

When **1** was heated in acetic acid containing 0.1 M perchloric acid and 0.24 M water at 114 °C for 30 min, it reacted completely and gave a mixture containing about 33% of **5**, 22% of **6**, and 45% of **7**. This experiment showed that **1** was reactive, but the conditions are severe enough that it seemed likely that some or all of these products were not those of kinetic control in the ring-opening addition reaction.<sup>7</sup> A reaction run at room temperature with 0.11 M perchloric acid in acetic acid (containing a small amount of acetic anhydride) for 4.5 h gave (<sup>1</sup>H

NMR analysis) about 50% reaction with a ratio of about 5 parts of **8** and **9** to 4 parts of **7**. At this stage neither **5** nor **6** was apparent. The reaction was allowed to continue, with aliquots taken from time to time. After 9 h, a trace of **5** appeared; the amount of **5** grew, after the **1** was consumed, at the expense of **8** and **9**, while the amount of **7** remained constant.

Even after 200 h, no trace of **6** appeared, and **10** and **11**, which may be progenitors of **6** (see below), were also not detected, either in early or late experiments. Compound **12**, which is a possible product of ring opening and which would be stable under these experimental conditions,<sup>8</sup> was also not detected.

At the end of the experiment (200 h), the ratio of **8**:**9** was 33:67. It seemed likely, in view of previous work,<sup>7,9</sup> that the *exo* isomer **8** was formed first and was converted rapidly in the acid medium to the equilibrium mixture with **9**. This likelihood was increased by a study of the acetolysis of **13** in the presence of sodium acetate, which led, via the Wagner-Meerwein rearrangement common to these ring systems,<sup>9a</sup> to the *exo* isomer **8**. **8** was found to have a half-life for equilibration with **9** in 0.01 M perchloric acid in acetic acid of a few hours at 41 °C. The half-life for rearrangement of the **8**-**9** mixture, which went cleanly to **5** (no **6** being formed at room temperature), was 135 h at room temperature (25 ± 2 °C) in