

## SKIPPED DIYNES—VII

### STEREOSPECIFIC THERMAL ISOMERIZATION OF A TETRAETHYNYLDIMETHYLENOCYCLOBUTANE\*

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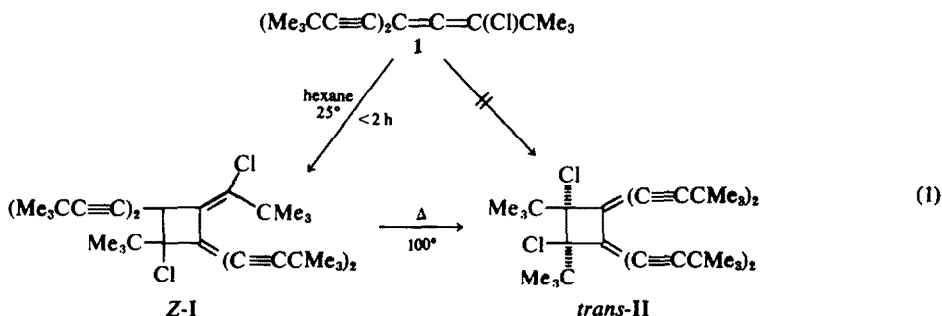
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**Abstract**—1,1-Bis(t-butylethynyl)-3-t-butylchloroallene (**I**) dimerizes stereospecifically at *ca* 25° to give *Z*-1-(t-butylchloromethylene)-2-bis(t-butylethynylmethylene)-3-t-butyl-3-chloro-4,4-bis(t-butylethynyl)cyclobutane (*Z*-**I**). At 100° *Z*-**I** rearranges to *trans*-3,4-dichloro-1,2-bis(bis(t-butylethynylmethylene))-3,4-di-t-butylcyclobutane (*trans*-**II**). The isomerization is first order in *Z*-**I** in the solvent bis(2-ethoxyethyl) ether. Rate data for 100° are  $k = 111 \times 10^{-6} \text{ sec}^{-1}$ ,  $\Delta H^\ddagger = 30.8 \pm 1 \text{ kcal/mole}$  and  $\Delta S^\ddagger = 15 \pm 3 \text{ eu}$ . It is proposed that the dimerization of **I** produces a bisallyl diradical in an orthogonal conformation from which conrotatory paths lead to *Z*-**I** or *trans*-**II**. The observations on this system are used to construct a useful, if simplistic, approach to rationalize or predict product distributions in reactions such as allene dimerizations, 1,2-dimethylenecyclobutane rearrangements, etc, which proceed through the bisallyl diradical. On the graph which connects all of the species (or on the energy surface which contains all of the species) the first products should be those which are one allowed reaction step away from a given diradical. Applications and exceptions to this concept of favored kinetic control are discussed.

The mechanisms by which dimethylenecyclobutanes interconvert and the energy surfaces on which these changes occur have attracted widespread interest. We report here an example of such a rearrangement involving a highly-substituted, sterically-hindered dimethylenecyclobutane. In the accompanying paper, we reported that the reaction of *tris*(t-butylethynyl)carbinol with phosphorus trichloride led exclusively to a single dimeric chloride (*Z*- or *seqcis*-**I**) by way of the chloroallene (**I**):<sup>1</sup>

Rarely do allenes yield a single dimer.<sup>2,3</sup> 1,1-Diphenyl-3-benzhydrylallene is analogous to **I** in that one dimer is formed under kinetic control (*ca* 110°) and a second is formed under thermodynamic control (*ca* 200°).<sup>4</sup> The apparent simplicity of this example and of process 1 is deceptive: disregarding optical isomers, fourteen dimeric structures are possible.<sup>1</sup> Admittedly, there is no example on record of a substituted allene that leads to a 1,3-dimethylenecyclobutane, so that these forms may be eliminated.<sup>2,3</sup> But when substituted allenes,



Upon heating to higher temperatures (*ca* 100°), **I** is quantitatively isomerized to a single isomeric dimer, **II**.

e.g., methylallene, trimethylallene, 1,2-cyclonadiene, 1-chloro-3-mesityllallene, etc, dimerize, they usually lead to mixtures of 1,2-dimethylenecyclobutanes.<sup>2,3</sup> Our system and process 1 are somewhat unusual, therefore, and we undertook a rate study of the isomerization of **I**. As a result we have gained new insight into the general questions of selectivity, mechanisms, and ener-

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getics both for the formation of allene dimers and their interconversions.

### RESULTS

The kinetics of the isomerization  $I \rightarrow II$  are clearly first order in the solvent *bis*(2 - ethoxyethyl) ether at 86–118°. The rate data are given in Table 1 and illustrated by typical plots in Fig 1. Activation parameters were obtained from least squares fits of these data to standard Arrhenius ( $A$ ,  $E_a$ ) and Eyring ( $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$ ) expressions. For a thermal reorganization of this type  $\Delta H^\ddagger$  is remarkably low and  $\Delta S^\ddagger$  is somewhat high—we shall comment on them after analysis of the mechanism.

**Mechanism.** The bulk of the evidence indicates that the conversion, allene to dimethylenecyclobutane, occurs by a multistep route in which the first intermediate is a 2,2' - bisallyl diradical.<sup>3,5</sup> According to theoretical calculations, which are not regarded as definitive,<sup>6</sup> the orthogonal ( $D_{2d}$ ) is slightly favored over the planar ( $D_{2h}$ ) form and the highest occupied (HO) and lowest unoccupied (LU)

molecular orbitals are ordered as in Fig 2. Given the disposition  $(b_3)^2 (b_2)^2 (b_1)^2 = {}^1A$ , one would predict disrotatory closure for planar and conrotatory closure for orthogonal forms; given the somewhat less probable distribution  $(b_3)^2 (b_2)^2 (a)^2$ , one would predict conrotatory closure for planar and disrotatory closure for orthogonal forms.<sup>6</sup> Recent workers generally favor conrotatory closure from the orthogonal conformations,<sup>7-11</sup> an option which is least equivocal in the unsubstituted diradicals.<sup>7</sup> For the case at hand (Eq 1), our open-ended analysis of numerous choices available in the formation, isomerisation, or collapse of the bisallyl diradical,

Table 1. Rate data and activation parameters for the isomerization,  $Z-I \rightarrow trans-II$  in the solvent  $(C_2H_5OCH_2CH_2)_2O^a$

Temp. °C	[Z-I] <sub>0</sub> 10 <sup>2</sup> × mol/l	k × 10 <sup>3</sup> sec <sup>-1</sup>
86.0	4.12	2.25
	2.66	2.36
99.8	2.75	10.34
	3.44	10.99
	3.57	11.90
117.5	2.50	73.05
	3.55	73.77
	3.55	79.30

Activation parameters <sup>a</sup>			
log A (sec <sup>-1</sup> )	E <sub>a</sub> (kcal/mole)	ΔH <sup>‡</sup> (kcal/mole)	ΔS <sup>‡</sup> (e.u.)
14.42	31.58 ± 0.17	30.84 ± 0.13	14.6 ± 0.3

<sup>a</sup> The number of significant figures given is simply intended to facilitate reproduction of our activation parameters. The indicated uncertainties are probable errors derived from a standard least squares treatment. We believe that more realistic uncertainties would be 5% in  $k$ , ± 1 kcal in  $\Delta H^\ddagger$  and  $E_a$ , and 2.3 e.u. in  $\Delta S^\ddagger$ .

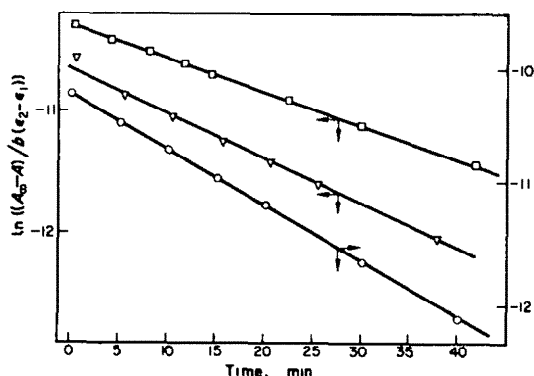


Fig 1. Rate data for the isomerization  $Z-I \rightarrow trans-II$  in  $(C_2H_5OCH_2CH_2)_2O$ :  $\Delta$ , 86°, time scale  $\times 24$ ;  $\square$ , 99.8°, time scale  $\times 4$ ;  $\circ$ , 117.5°, time scale as shown.

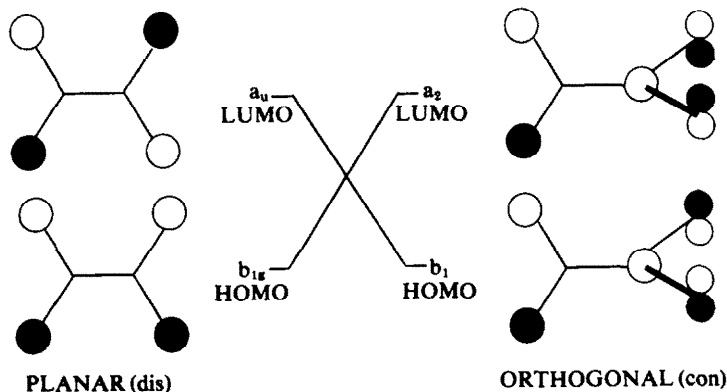


Fig 2. Highest occupied and lowest unoccupied molecular orbitals (HOMO, LUMO) of planar ( $D_{2h}$ ) and orthogonal ( $D_{2d}$ ) forms of the 2,2'-bisallyl radical, according to Ref 6. The orientation in the closure of the biradical to 1,2-dimethylene-cyclobutane is indicated as dis or con, depending on orbital symmetry.

leads almost inevitably to the same preference, that is, conrotatory closure of the orthogonal diradical.

Let us begin with the possible diradicals that may be formed from the allene (1). Three orthogonal conformations designated as **RI**, **RII** and **RIII**, may be conveniently represented by the modified Newman-Fischer projections of Fig 3. Since the diradicals are chiral, conrotatory closures of each one and its enantiomer may lead to diastereoisomers. But because the set, **RI**, **RII** and **RIII**, or the set of their enantiomers leads to the "same" group of products, allowing for the fact that some products may be enantiomeric, we need only work with three orthogonal radicals. By simple rotations, these **R** lead to six planar conformations, **P**, pictured in Fig 4.

If relatively free rotation about the central bond (2,2') and an end bond (e.g., 1,2) were possible, all bisallyl diradicals and presumably all dimers would become accessible. However, a 2,2' rotation (180°) merely interconverts the enantiomeric pairs of **R** and 1,2 rotations (180°) interconvert **RI**, **RII** and **RIII**. Likewise, 2,2' rotation (180°) interconverts pairs of **P**, but 1,2 rotations (180°) connect **PI**, **PII** and **PIII**. Not much is known about the rotation barriers in such cases. Theoretical calculations on bisallyl indicate that the  $D_{2d}$  form is somewhat more stable than the  $D_{2h}$  form by *ca* 4 kcal/mole and that a *ca* 40° twisted form is slightly more stable than the  $D_{2d}$  form.<sup>6</sup> Since rotational barriers of the order of 10 kcal/mole have been estimated for simple

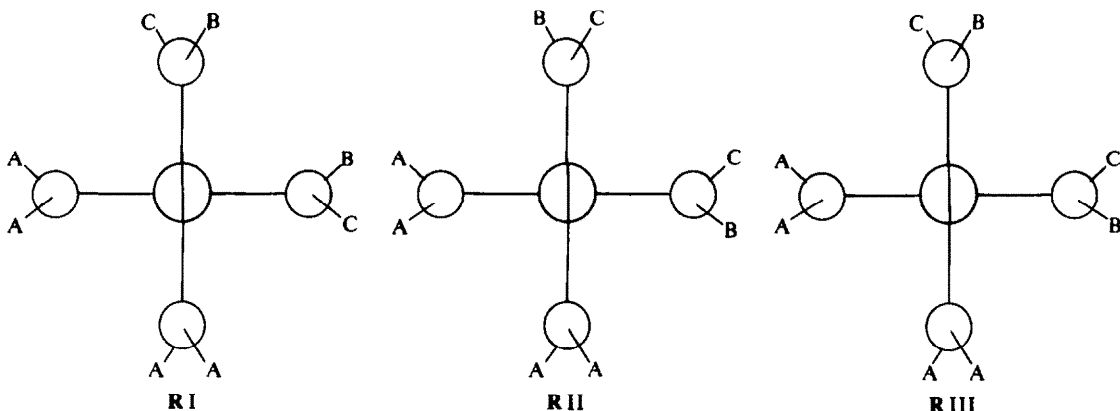


Fig 3. Orthogonal 2,2'-bisallyl diradical conformations (A = *t*-butylethynyl, B = *t*-butyl, C = chlorine).

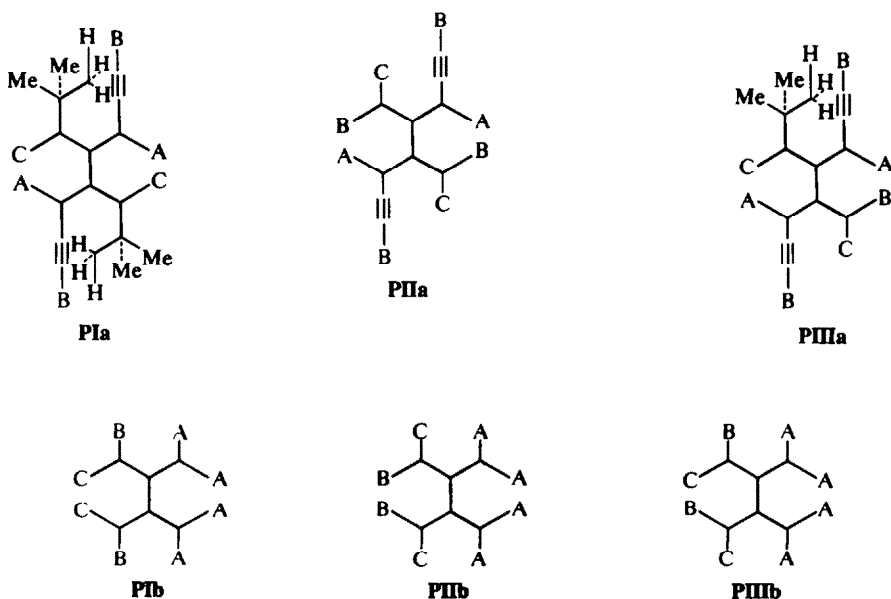


Fig 4. Conformations of planar 3,3'-bisallyl diradicals (A = *t*-butylethynyl, B = *t*-butyl, C = chlorine) and typical *t*-butyl vs *t*-butylethynyl steric interactions.

1,4-diradicals,<sup>12</sup> barriers for 2,2' or 1,2 bonds in bisallyl, and especially in substituted bisallyls, should be substantially higher. Because the rotation of an end carbon involves the loss of allylic stabilization (*ca* 10.5 kcal/mole),<sup>13</sup> the 1,2 barrier should be greater than the 2,2' barrier. Perhaps the most useful information comes from a report on the degenerate rearrangements of *cis*- and *trans*-3,4-dimethyl-1,2-dimethylenecyclobutane: both middle and end carbon rotations are slow processes, that is,  $k_{\text{rotation}} \ll 0.2 k_{\text{collapse}}$  for the bisallyl radical. We can be confident, therefore, that in substituted bisallyl, where barriers should be higher, collapse to dimers is faster than equilibration of the RI (or PI) pair, which in turn is faster than interconversion among RI, RII, and RIII (or PI, PII, and PIII).

Consideration of steric effects allows one to roughly arrange the diradical conformations according to their energies. From the partial structures given in Fig 4 and even more obviously from scale models, one finds that in PI and PIII, a *t*-Bu (B) group and an ethynyl group (A) must either occupy the same space or the molecule must become seriously distorted. On this basis, we believe that the energies would decrease in the order PI > PIII > PII. Rotation of the planar to orthogonal

forms does not alter the gross interference of B and A in 1,3- or 1',3'-positions (Fig 4) and thus the energies would decrease in the order RI > RIII > RII. Finally, scale models clearly show that the 1,1' and 3,3' steric interactions in P are always attenuated or relieved in R forms. One could, on this basis alone, argue that the planar diradicals were far less likely than the orthogonal diradicals as intermediates. Moreover, since there is no apparent orbital restriction on the formation of bisallyl from two allene molecules, one might guess that RII would be favored.

In general, any planar bisallyl can close on four disrotatory and any orthogonal bisallyl can close on four conrotatory least motion paths (Fig 2). For diradicals derived from an allene of the structure 1, the number of allowed paths is considerably less: the orthogonal diradicals collapse by ten paths to seven products, which we label (*Z* or *E*)-I, (*trans* or *cis*)-II and (*Z,Z* or *E,E* or *E,Z*)-III and pictured in the accompanying paper (enantiomers are not considered here).<sup>1</sup> All of the connected species are set down in Table 2 or in *graphs* (Fig 5).<sup>14</sup> Since only *Z*-I and *trans*-II show up in this work (Eq 1), we assume that any path that does not include both of them may be excluded. This limits the

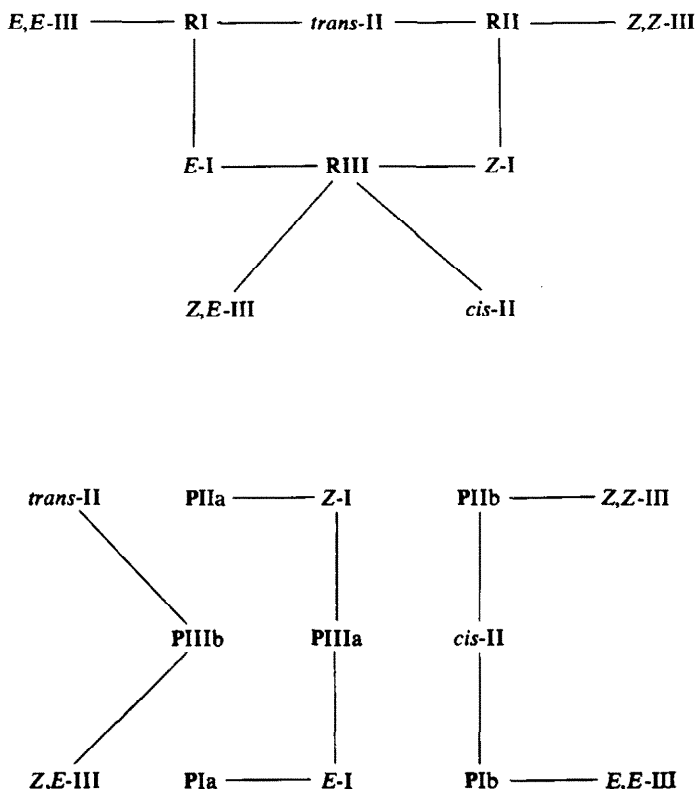


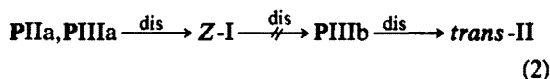
Fig 5. Itineraries in 1,2-dimethylenecyclobutane interconversions: upper graph, orthogonal bisallyl diradicals (R) and conrotatory paths; lower graphs, planar bisallyl diradicals (P) and disrotatory paths.

Table 2. Orbital symmetry allowed processes for dimerization of allene **1** and interconversion of dimers

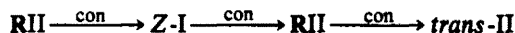
	Planar forms <b>P</b>		Orthogonal forms <b>R</b>	
	Rotation	Product <sup>a</sup>	Rotation	Product <sup>a</sup>
Ia	dis	<i>E</i> -I	I con	<i>E</i> -I
Ib	dis	<i>cis</i> -II	con	<i>trans</i> -II
	dis	<i>E,E</i> -III	con	<i>E,E</i> -III
IIa	dis	<i>Z</i> -I	II con	<i>Z</i> -I
IIb	dis	<i>cis</i> -II	con	<i>trans</i> -II
	dis	<i>Z,Z</i> -III	con	<i>Z,Z</i> -III
IIIa	dis	<i>Z</i> -I	III con	<i>Z</i> -I
IIIb	dis	<i>E</i> -I	con	<i>E</i> -I
	dis	<i>trans</i> -II	con	<i>cis</i> -II
	dis	<i>Z,E</i> -III	con	<i>Z,E</i> -III

<sup>a</sup>The structures of the product 1,2-dimethylenecyclobutanes are given in the accompanying paper.<sup>1</sup>

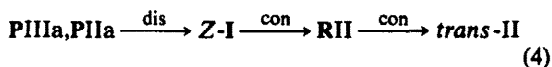
itineraries: *via P* radicals there is no path,



*via R* radicals,



and *via P* and *R* radicals,



which is just one of several "mixed" itineraries which can be formulated, if the separate graphs of Fig 5 are united. Conrotatory paths from RII (Eq 3) or RIII (not shown) to *Z*-I satisfy all of the requirements simply. Since all of the 2,2'-bisallyl diradicals are, *a priori*, equally accessible from the allene (**1**), favored formation of RII over RIII would reflect the ordering of the radicals on the basis of stability. For this reason, we regard the mixed sequence (Eq 4), which is properly selective, as unlikely, because PIIa should fall down the energy surface into the stable conformation of RII.

To summarize, we propose that the first step in the dimerization of the allene yields RII which closes in the conrotatory sense at *ca* 25° to yield *Z*-I or at *ca* 100° to yield *trans*-II; at *ca* 100° *Z*-I opens in the conrotatory sense to re-form RII which then closes to form *trans*-II. Because of numerous assumptions made in its evolution, we cannot regard this preferred sequence (Eq 3) as absolutely determined. Certainly, it is useful for our system and has applications in other systems, as we shall see.

**Energetics.** Since  $E_a = 63$  kcal/mole for the ring opening of cyclobutane and  $E_a = 49$  kcal/mole for the ring opening of methylenecyclobutane, Doering and Dolbier thought that the energy difference

could perhaps be attributed to allylic stabilization of the second activated complex.<sup>15</sup> If the same decrement held for the ring opening of 1,2-dimethylenecyclobutane,  $E_a$  should be *ca* 35 kcal/mole; if the strain energy of exomethylene groups were included, this estimate would be reduced by *ca* 26 kcal/mole.<sup>16</sup> In this product-like model for the activated complex, we have a lower limit which is far below the observed  $E_a = 46.5$  kcal/mole (Table 1). If, for our system, we use 46.5 kcal/mole as a starting point and take into account the extra stabilization of *ca* 2 or 4.5 kcal/mole, respectively, that is observed when an alkyl or vinyl group is attached to the end of any allyl radical,<sup>13</sup> the estimate would be  $E_a \geq 46.5 - 2(2) - 4(4.5) = 22.5$  kcal/mole. Since we find  $E_a = 31.6$  kcal/mole, we attribute the reduction from 46.5 to 31.6 in  $E_a$  to extensive but incomplete conjugation in the activated complex and to some release of steric strain in the reactant dimer *Z*-I.

Our pre-exponential (*A*) factor appears to be quite normal (Table 1). If, however, one compares  $\Delta S^\ddagger = 15$  eu with others for ring opening,<sup>16,17</sup> it appears that our value is high. Undoubtedly this reflects an easing of the constraints on some of the bulky groups in *Z*-I.

Our proposal for the reaction coordinate for processes 1 and 3 is given schematically in Fig 6. The energy assignments are partly supported by our observations and partly based on analogies.<sup>7,13</sup> Since *trans*-II is more stable than *Z*-I, we assume that  $\Delta\Delta H_{1,11} \geq 2.5$  kcal/mole. Following an argument of Gajewski and Shih,<sup>7</sup> we make  $2\Delta H(1) - \Delta H(\text{RII}) \approx 0 \pm 5$  kcal/mole. Our observations require that the

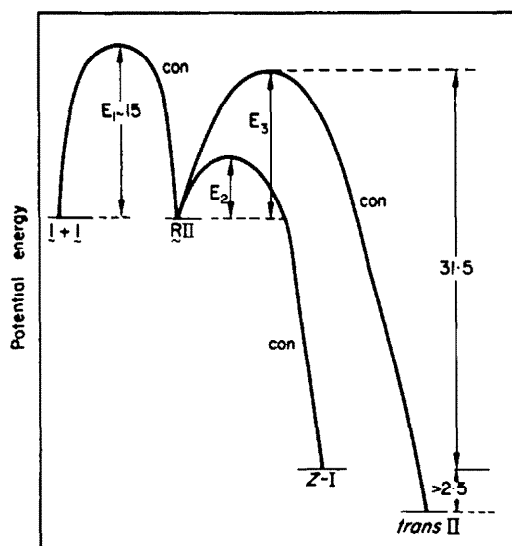
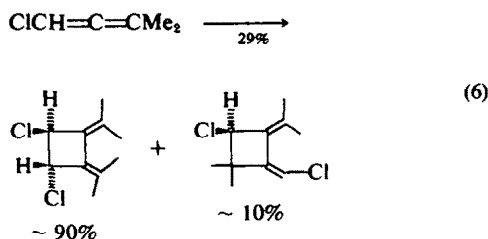
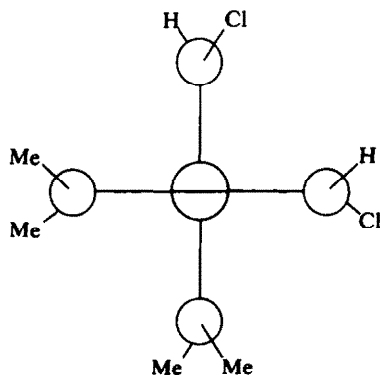
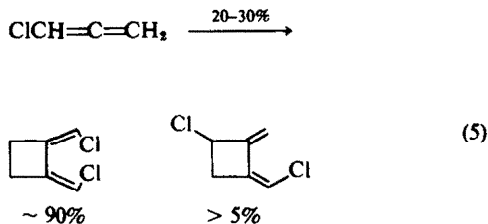
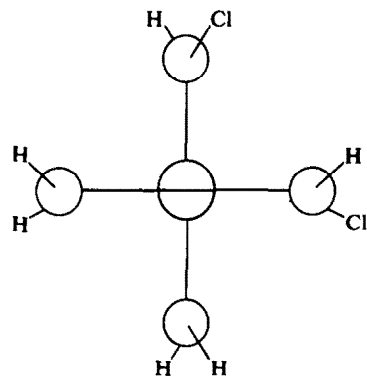


Fig 6. Proposed energy surface (schematic) for formation of *Z*-I and its isomerization to *trans*-II. Numerical values in kcal/mole.

energy maximum lies on the path connecting Z-I and *trans*-II, according to Eq 3. As for the initial step, we know that allene 1  $\rightarrow$  Z-I in *ca* 2 h at 30° and that  $\Delta H^\ddagger = 16.8$  and  $\sim 11$  kcal/mole for the dimerization of 1,3-diphenylallene<sup>11</sup> and tetrachloroallene,<sup>18</sup> respectively. Therefore, we guess  $E_a \approx 15 \pm 4$  kcal/mole for 1. Concerning the ring closures from RII,  $E_3$  is obviously greater than  $E_2$ , and it seems safe to set the upper limit  $E_3 \approx 10$  kcal/mole.<sup>12</sup> This completes the energy surface for our system as far as we can give it at present.

**Applications.** We wish to explore the notion that one can often account for the "first" products of thermal allene dimerizations by assuming that one bisallyl diradical is preferentially formed and that it alone yields the first dimers. For the present we assume orthogonal diradicals and thermal conrotatory processes, but analogous schemes could be formulated for planar radicals or other conditions. Here the products are limited to 1,2-dimethylenecyclobutanes but other isomers, e.g., methylenespiropentane, bicyclopopylidene, etc.,<sup>6,7a,19</sup> could be "first" as well. In essence then, we wish to see how far one can go with single reaction steps originating in a given diradical, e.g., R (or P) in Fig 5.

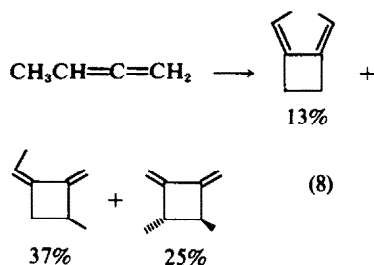
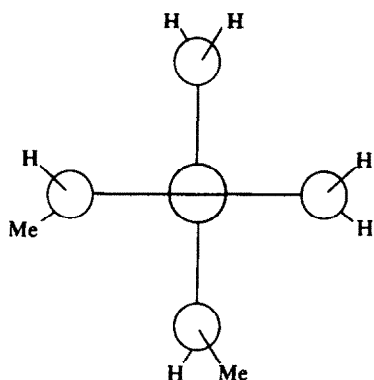
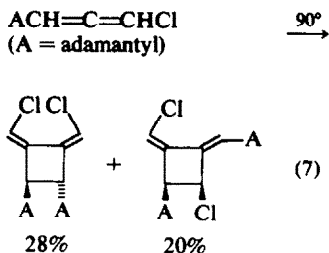
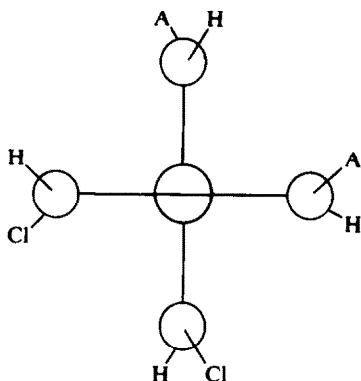
Qualitatively, the behavior of  $(\text{Ph})_2\text{C}=\text{C}=\text{C}=\text{C}=\text{C}=\text{C}$



$\text{CHCHPh}_2$ , closely parallels that of 1 in Eq 1 so that one key diradical can account for the products.<sup>4</sup> Several different examples, Eqs 5–8, from several sources, illustrate the approach further, e.g., the dimerization of chloroallene,<sup>8</sup> 1-chloro-3-methyl-1,2-butadiene,<sup>8</sup> 1-adamantyl-3-chloroallene,<sup>9</sup> and methylallene.<sup>7b</sup> In process 7, two additional products (20%, 3%) are not shown because the major one was probably formed under equilibrium control and the second was formed in low yield. According to our hypothesis, the ring substituents (Cl, A) in the last structure should be *cis*. Finally, the dimerization of triphenylallene almost fits the hypothesis: of the three products, two can be derived from one diradical.<sup>11</sup>

In Eqs 5–8, it was assumed that a diradical was formed from two allene molecules. The notion of first products would still apply if the diradical were formed from any dimer; that such is the case has been elegantly demonstrated for the *cis* or *trans*-3,4-dimethyl-1,2-dimethylenecyclobutanes.<sup>7a</sup> All of these examples support our hypothesis and should provide incentive for workers to attempt to use kinetic control to improve stereoselectivity in allene dimerizations.

We propose the idea of first dimers as a zero order hypothesis: simply consider the graph relev-



ant to the system at hand and favor those processes that begin at a given diradical.

Certainly, this has been considered<sup>3,8,9,11</sup> and applied before.<sup>7a</sup> Because allenes often produce a large number of dimers whose structures are not always certain,<sup>9,20</sup> the simplifying notion of both orbital symmetry and exclusive kinetic control has not been extensively explored. Of course, there are cases in which more than the first dimers are produced. Whether two or more diradicals are formed competitively from the allenes, by rotations in the radicals, or by successive ring opening-closure, cannot be decided by our simple approach. However, it does seem clear from the constancy of the product distribution that 2,3-pentadiene yields its dimers on at least two kinetically competitive paths, presumably *via* two or more diradicals.<sup>10</sup> Likewise, two competitive paths are probably involved in the dimerization of the 1,2-cyclo-nonadienes<sup>21</sup> and are most certainly involved in the dimerization of allene itself.<sup>3</sup>

#### EXPERIMENTAL

**Materials.** Z-I was recrystallized from acetone and dried under vacuum before use. The solvent *bis*(2-ethoxyethyl) ether (BEE) was stored over NaOH for 24 h, filtered through MgSO<sub>4</sub>, refluxed over Na for 4 h, and fin-

ally distilled under vacuum: b.p. 76–78° (12 mm). Tests for peroxide in BEE were made either with KI or ferrous thiocyanate. Immediately before use, BEE was shaken with sodium hydroxide pellets for 10 min, filtered successively through a cone of pre-dried alumina and through a cone of activated charcoal; peroxides were completely eliminated by this procedure and the solvent could be routinely handled in air for *ca* 4 h before it gave a positive peroxide test. Water, 1,2-dimethoxyethane and *n*-butanol were fractionally distilled to give cuts of constant b.p., which were used as bath fluids.

**Kinetic procedures.** Measurements were made at 3 temps in a bath consisting of a 3 l flask filled with 2 l of refluxing solvent. The flask was wrapped with several layers of glass wool and protected from drafts during runs. The temp variation of the bath was found to be less than 0.2° over long periods of time (48 h). A soln of Z-I in BEE made up to the desired concentration was distributed among several ampoules (2 ml capacity) and these were sealed either in air or under vacuum. Upon opening, ampoules sealed in air inevitably gave a positive peroxide test. However, a run with peroxide-free solns showed no change in the rate within experimental error compared to peroxide-containing solns. For normal runs, then, the ampoules were filled in the atmosphere, cooled to –80°, and sealed with a torch. For peroxide-free runs, the ampoules were filled in air, degassed (0.2 mm) by repeated freezing and thawing, cooled to –80°, and sealed under vacuum. These filled ampoules were then left in the bath for the allotted interval after which they were removed,

quenched in a  $-20^\circ$  ice-salt bath and analyzed.

The rate of formation of *trans*-II ( $\epsilon_1 \approx 20400$ ) from pure Z-I ( $\epsilon_2 \approx 2500$ ) was measured by following the UV absorption at 364 nm. Their spectra are given in Fig 7. Beer's Law was found to hold for both Z-I and *trans*-II in a 1.0 cm quartz cell over the concentration range  $0.00 - 4.19 \times 10^{-3}$  M in BEE. The reactions were followed for ca 4 half-lives and the optical density (A) at infinite time was measured after 10 half-lives. The rate law appropriate to our work was

$$\ln((A_\infty - A)/b(\epsilon_2 - \epsilon_1)) = \ln[Z-I]_0 - kt \quad (9)$$

in which b is the cell length and  $[Z-I]_0$  the initial concentration of Z-I.

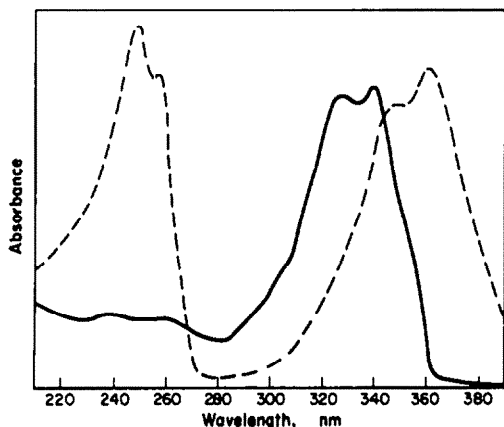


Fig 7. Absorption spectra of Z-I (—) and *trans*-II (----).

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