acetate were used (Table I), and each run was done in duplicate. The rate constants were identical within probable error, and were averaged. Table II provides data for a typical run.

The methanolysis rates were measured on tosylate (−)-IV prepared from alcohol (−)-V with $[\alpha]^{25}_{546}$ −52.3° (*c* 0.98, $CHCl_3$). The solution was unbuffered, and was 15% (by volume) chloroform that had been freed of ethanol. The two first-order least-squares rate constants obtained by following the reaction at two wavelengths were the same within experimental error (see Table I).

**Titrimetric Kinetics.** The procedure described previously[6,24] was applied to racemic 1-tosyloxy[2.2]paracyclophane, mp 88° dec. *Anal.* Calcd for $C_{23}H_{22}O_3S$: C, 72.97; H, 5.87. Found: C, 73.02; H, 6.04.[5] The conditions and results are reported in Table I.

---

(24) D. J. Cram and F. L. Harris, *J. Amer. Chem. Soc.*, **89**, 4642 (1967).

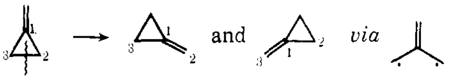
# Hydrocarbon Thermal Degenerate Rearrangements. IV. The Stereochemistry of the Methylenecyclopropane Self-Interconversion. Chiral and Achiral Intermediates[1]

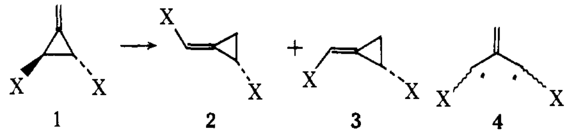
**Joseph J. Gajewski**

*Contribution No. 1976 from the Department of Chemistry,*
*Indiana University, Bloomington, Indiana 47401.* *Received September 4, 1970*

**Abstract:** Under conditions of kinetic control, *trans*- and *cis*-2,3-dimethylmethylenecyclopropanes, **5** and **6**, respectively, were interconverted thermally with rates comparable to those for rearrangement to the same 7:1 mixture of *anti*- and *syn*-2-methylethylidenecyclopropanes, **9** and **10**, respectively. Pyrolysis of optically active **5** gave inverted **9** as well as optically active **10** of the same sign and magnitude of rotation as that of **9**. Racemization of optically active **5** was twice as fast initially as calculated for reversible formation of **5** from **6**. Orthogonal trimethylenemethane diradical intermediates are proposed to account for the interconversion of **5** and **6** as well as formation of inverted **9** and **10**, and excess racemization is attributed to intervention of achiral, either planar or bisorthogonal, trimethylenemethane diradicals. The energetics and stereochemical features of the rearrangement and of the intermediates are discussed, and the suggestion is made that the orthogonal diradicals are at least 12 kcal/mol more stable than the planar or bisorthogonal diradicals.

Methylenecyclopropanes are known to undergo thermal self-interconversions by cleavage of the allylic bond and bond formation between an original ring carbon and the original exocyclic methylene carbon.[2] The transition state or intermediate in the reaction is most likely a trimethylenemethane diradical.[3] However, it is the geometry of this species involved in this degenerate rearrangement that is of concern. Feist's ester, **1**, has long been known to undergo this rearrangement. Ullman demonstrated that optically active products, **2** and **3**, were formed when the starting ester was optically active.[2a] This observation precludes the sole intervention of an achiral intermediate such as planar **4**. More recently Doering and Roth have determined the absolute configurations of **1**, **2**, and **3** involved in the thermolysis and found inversion of configuration at the remaining chiral center in **2** and **3** when produced from **1** as depicted above.[2g] Significantly, there was little *trans*-**1** to *cis*-**1** isomerization and even *cis*-**1** gave **2** and **3** with formation of only small amounts of *trans*-**1** kinetically.

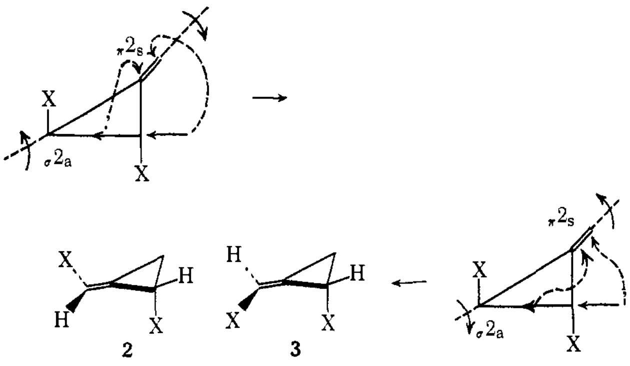




1 2 3 4

X = $CO_2CH_3$

These facts have been cited by Woodward and Hoffmann[4] as being consistent with an orbital symmetry allowed ${}_{\pi}2_s + {}_{\sigma}2_a$ sigmatropic shift in the methylenecyclopropane degenerate rearrangement. There are



2 3

---

(1) (a) For part III, see J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **91**, 5900 (1969). (b) For a preliminary report of this work, see J. J. Gajewski, *ibid.*, **90**, 7178 (1968).

(2) (a) E. F. Ullman, *ibid.*, **81**, 5316 (1959); (b) J. P. Chesick, *ibid.*, **85**, 2720 (1963); (c) J. C. Shields, B. A. Shoulders, J. F. Krause, C. L. Osborn, and P. D. Gardner, *ibid.*, **87**, 3026 (1965); (d) J. K. Crandall and D. R. Paulson, *ibid.*, **88**, 4302 (1966); (e) J. C. Gilbert and J. R. Butler, *ibid.*, **92**, 2168 (1970); (f) D. R. Paulson, J. K. Crandall, and C. A. Bunnell, *J. Org. Chem.*, **35**, 3708 (1970); (g) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

(3) For alternative sources of this diradical, see: (a) P. Dowd, A. Gold, and K. Sachder, *J. Amer. Chem. Soc.*, **90**, 2715 (1968); (b) R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966); (c) P. S. Skell and R. G. Doerr, *ibid.*, **89**, 4688 (1967); (d) S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966).

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

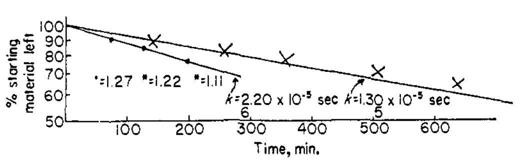


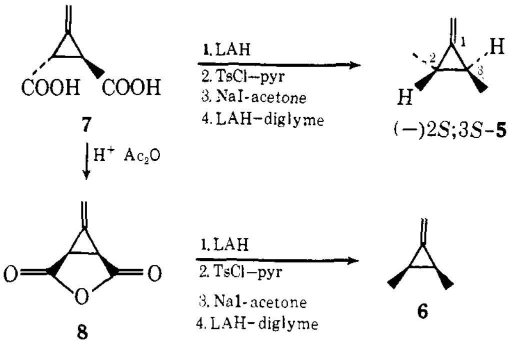
Figure 1. Log plot of per cent decomposition of **5** and **6** at 152.0°: ×, per cent **5** left; ●, per cent **6** left; *, **5**/**9** + **10** from **6**; *k* in $sec^{-1}$.

two electronically allowed pathways, each one of which is responsible for one or the other of the $\alpha,\beta$-unsaturated ester products.

Previous to the announcement of Doering's study, we[1] reported that the stereochemistry of the 2,3-dimethylmethylenecyclopropane thermal rearrangement occurred with inversion at the migrating carbon and that geometric (cis to trans) isomerization was competitive with rearrangement—results consistent with a diradical pathway involving chiral species. Further, we reported that an achiral intermediate was also accessible on the energy surface for this reaction. We here give the full details of this work with more recent experiments that substantiate the original results, certain assumptions, and conclusions. In addition, a reinterpretation of the energy surface for this methylenecyclopropane rearrangement is provided.

## Results

***trans*- and *cis*-2,3-Dimethylmethylenecyclopropanes.** *trans*- and *cis*-2,3-Dimethylmethylenecyclopropanes, **5** and **6**, respectively, were prepared from *trans*-Feist's acid[5] and the corresponding *cis*-anhydride,[6] **7** and **8**, respectively, by lithium aluminum hydride reduction, tosylation, iodide displacement, and lithium aluminum hydride displacement.



**7**

(−)2*S*;3*S*-**5**

**8**

**6**

Optically active **5** was obtained from **7** which was resolved with brucine; $[\alpha]^{22}\text{D}$ (of **5**) −59.4° ($CCl_4$) when derived from **7** of $[\alpha]^{22}\text{D}$ −149.4° (EtOH). Dextrorotatory, optically pure, Feist's acid, $[\alpha]_{546}$ +176° (EtOH), has been shown by Doering[2g] to be of the *R* configuration (the opposite of that shown above).

**Products Derived from Pyrolysis of 5 and 6.** ***anti*- and *syn*-2-Methylethylidenecyclopropanes.** Preliminary vapor phase pyrolyses of **5** and **6** in sealed tubes in the temperature range of 170–255° revealed that **5** and **6** were interconverted with one another as well as with two other materials which were presumed to be the *anti*- and *syn*-2-methylethylidenecyclopropanes, **9** and **10**, respectively. These latter materials originally could only be separated by capillary analytical vpc, so authentic samples were prepared from the *anti*- and *syn*-2-carbethoxyethylidenecyclopropanes, **11** and **12**, respectively, by the same reaction sequence that allowed conversion of **7** to **5** and **8** to **6**. The stereochemistries of **11** and **12** were determined previously,[7] and, indeed, **9** and **10** derived from these were the same as those produced upon pyrolysis of **5** and **6**.

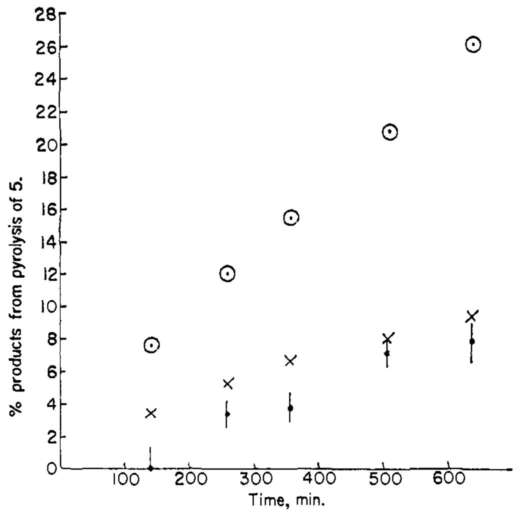
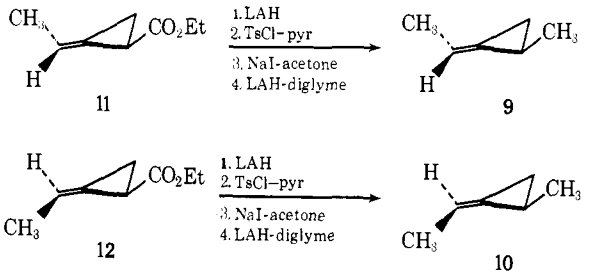


Figure 2. Per cent of products from pyrolysis of **5** as a function of time at 152.0°: ⊙, per cent of **9** + **10**; ×, per cent of **6**; ɫ, per cent racemization of **5**.



**11**

**9**

**12**

**10**

**Thermal Equilibration of 5, 6, 9, and 10.** In the temperature range 230–255° the vapor of **5** and **6** in sealed tubes gave a mixture of **5**, **6**, **9**, and **10** in the ratio 2:1:12:12 after 1–1.5 hr. Heating this equilibrated mixture for 1 week at 150° gave a mixture of **5**, **6**, **9**, and **10** in the ratio of 2.5:1:19.3:17.7, respectively.

**Pyrolysis of 6 and Optically Active 5 for Short Reaction Times.** Optically active **5** ($[\alpha]^{22}\text{D}$ −57.6° ($CCl_4$)) and **6** were subjected to vapor-phase pyrolysis in a 200-ml well-conditioned static reactor at 152.0°. The reactor was attached to a standard vacuum line for introduction and removal of samples. Sample sizes varied from 10 to 100 μl and pyrolysis times were carefully noted. The recovered samples were analyzed by capillary vpc and nmr and the data are presented in Figures 1 and 2.

The optical rotation of recovered **5** was determined after preparative vpc separation, and these data are also given in Figure 2. The vpc fractions containing **9** and **10** from these reactions were combined and found to have a D-line rotation of +12.0° ($CCl_4$). After careful vpc separation of this mixture to remove **10**, the re-

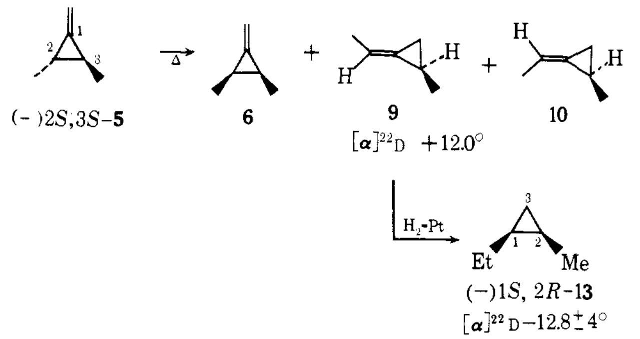
---

(5) F. Feist, *Ber.*, **26**, 750 (1893).

(6) M. G. Ettlinger and F. Kennedy, *Chem. Ind.* (*London*), 222, 492 (1954).

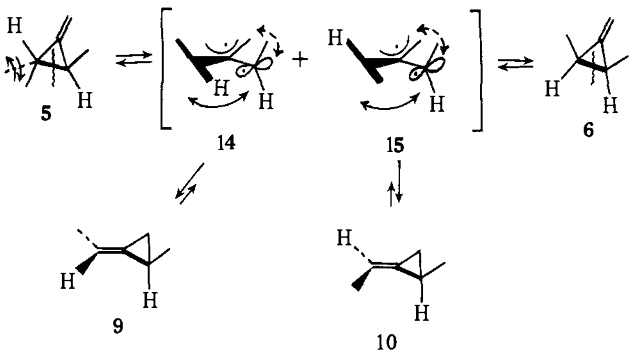
(7) J. J. Gajewski and L. T. Burka, *J. Org. Chem.*, **35**, 2190 (1970).

maining **9** had a D-line rotation of +10.7 ± 1.0°, suggesting that **10** also had a substantial rotation in a positive sense. When this sample of **9** was hydrogenated over platinum catalyst, a small amount of *cis*-1-ethyl-2-methylcyclopropane (**13**) with $[\alpha]^{22}\text{D}$ −12.8 ± 4° (isooctane) was obtained. The absolute configurations of **5** (*vide infra*) and **13**[8a] [(−)-1*S*,2*R*] are known and correspond to those in the scheme below. Thus, there is inversion at the migrating carbon in the formation of **9**. The maximum rotation of **13** is also known,[8a] and the material derived from the pyrolysis–hydrogenation sequence is therefore at least 80 ± 20% optically pure.[8b] In pyrolyses conducted in sealed tubes at 170°, **5** $[\alpha]^{22}\text{D}$ −59.4° ($CCl_4$) gave a mixture of **9** and **10** in the ratio of 7:1 with D-line rotations of +13.6, +12.7, and +11.5° after 16, 37, and 58.5% disappearance of **5**, respectively, indicating that **9** and **10** are either racemizing under the reaction conditions or being produced from achiral species which are formed as the reaction proceeds, or both.



## Discussion

**Gross Mechanism.** From the above data, geometric isomerization of **5** and **6** occurs at a rate comparable to that of rearrangement to **10** and inverted **9**. The data also indicate that **10** produced in the rearrangement has the same, if not larger, positive rotation as **9**, strongly suggesting that **10** is also of inverted configuration. The simplest gross mechanistic hypothesis for this methylenecyclopropane self-interconversion that accounts for the facts involves homolytic cleavage of the allylic bond with a single 90° rotation about one of the cyclopropane bonds to give either of the orthogonal trimethylenemethane diradicals, **14** or **15**. Each of these diradicals is chiral and can re-form either **5** or **6** by the microscopic reverse of the process that formed them (solid double-headed arrow). Thus, if further rotation about bonds in **14** or **15** is slow compared to ring closure, optically active **5** will be re-formed from **14** or **15** if these were produced from optically active **5**. To the extent that **14** and **15** are formed from **6**, they must be a racemic mixture. Importantly, just as **14** can re-form **5** or **6**, it can give the anti material **9** (dotted double-headed arrow) but not the syn compound **10** unless further rotations about the allyl radical occur without bond formation. Similarly, **15** can form only **5**, **6**, and **10** but not **9**. If there were rotation about the allylic radical portion of **14** or **15**, the two could be interconverted and possibly racemized. However, to the extent that this allylic radical fragment resembles an ordinary allylic radical, a barrier to rotation of 12.6 kcal/mol[9] might be anticipated. Therefore, **14** and **15** are assumed to be configurationally stable with respect to the allylic radical portion.



An important point of this mechanistic hypothesis is that the ring closure is assumed to be the microscopic reverse of the ring opening; therefore, **14** and **15** will give **9** and **10**, respectively, by forming the new cyclopropane bond from the backside of the ring carbon which did not rotate in the initial cleavage. Thus inversion is the stereochemical result at that carbon upon rearrangement. This argument is based on a least motion principle, although there is the possibility that the trimethylenemethane singlet diradical has an overwhelming preference for an orthogonal geometry. These points will be taken up in detail subsequently.

In the scheme above, the formation of **9** from **14** and **10** from **15** are reversible reactions. However, at equilibrium, **9** and **10** are substantially favored over **5** and **6**; therefore, the formation of **14** and **15** from **9** and **10** must be slow relative to formation of **14** and **15** from **5** and **6**. This implies that during the first half-life for disappearance of **5** or **6** the formation of **9** and **10** is essentially irreversible, a point that will be utilized below.

The mechanistic hypothesis above then accounts for the geometric isomerization of starting materials **5** and **6** and the formation of inverted rearrangement products **9** and **10**. However, both starting trans material **5** and product **9** are partly racemized. Moreover, the extent of racemization increases as the extent of reaction increases. Since the achiral cis material **6** is formed and rearranges to **5**, **9**, and **10** under the reaction conditions, racemization of these materials is not unexpected. A kinetic analysis (below) of the reaction scheme provides both a justification for the anticipated consequence and the suggestion that there is still another achiral intermediate in the rearrangement.

**Kinetic Analysis. Intervention of Achiral Intermediates.** A reasonable kinetic scheme for the interconversions of the dimethylmethylenecyclopropanes during the first half-life for loss of active **5** (5a) is shown below. The reversal of **9** and **10** to **5** and **6** is not considered. To further simplify the analysis, racemic **5** (5r) is assumed to be formed irreversibly which is a good approximation at short reaction times. The pathway $k_2$ represents one for **5** to racemize without direct intervention of archiral **6** (see below). Thus, $d\mathbf{5}\text{a}/dt = -(k_1 + k_2 + k_3)\mathbf{5}\text{a}$; $d\mathbf{6}/dt = k_1\mathbf{5}\text{a} - (k_4 + k_5)\mathbf{6}$; $d\mathbf{5}\text{r}/dt = k_2\mathbf{5}\text{a} + k_4\mathbf{6}$; $d\mathbf{9},\mathbf{10}/dt = k_3\mathbf{5}\text{a} + k_5\mathbf{6}$. Integrating, these equations yield: 5a = exp((−

---

[8] (a) R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 7405 (1969). (b) This is a minimum value since the optical purity of **1** used here is not known. However, it must have been of high optical purity.[2g]

[9] K. W. Egger, D. M. Golden, and S. W. Benson, *ibid.*, **86**, 5420 (1964).

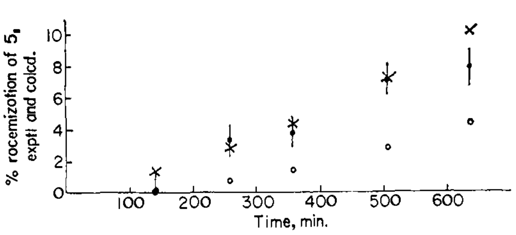


Figure 3. Per cent racemization of active **5** as a function of time at 152.0°: ♦, experimental; ×, calcd with $k_2 = 0.13 \times 10^{-5}\ \text{sec}^{-1}$; ○, calcd with $k_2 = 0$.

$k_1 - k_2 - k_3)t)$; $\mathbf{6} = (k_1/(k_4 + k_5 - k_1 - k_2 - k_3))\cdot(\mathbf{5}\text{a} - \exp((-k_4 - k_5)t))$; $\mathbf{5}\text{r} = (((k_1k_4)/(k_4 + k_5 - k_1 - k_2 - k_3))(((1.0 - \mathbf{5}\text{a})/(k_1 + k_2 + k_3)) - ((1.0 - \exp((-k_4 - k_5)t))/(k_4 + k_5)))) + ((k_2/(k_1 + k_2 + k_3))(1.0 - \mathbf{5}\text{a}))$; $\mathbf{9{,}10} = (-k_3/(k_1 + k_2 + k_3))\cdot(\exp((-k_1 - k_2 - k_3)t)) - (k_5/(k_1 + k_2 + k_3))(\exp((-k_1 - k_2 - k_3)t))(k_1/(k_4 + k_5 - k_1 -- k_2 - k_3)) + (k_5/(k_4 + k_5))(\exp((-k_4 - k_5)t))(k_1/(k_4 + k_5 - k_1 - k_2 - k_3)) + (k_3 + k_5(k_1/(k_4 + k_5 - k_1 - k_2 - k_3)))/(k_1 + k_2 + k_3) - (k_5(k_1/(k_4 + k_5 - k_1 - k_2 - k_3))/(k_4 + k_5))$.

$$\begin{tikzcd}
\mathbf{5}\text{a} \arrow[r, "k_1"] \arrow[d, "k_3"] \arrow[rr, bend left, "k_2"] & \mathbf{6} \arrow[r, "k_4"] \arrow[d, "k_5"] & \mathbf{5}\text{r} \\
\mathbf{9,10}\,\text{(act)} & \mathbf{9,10}\,\text{(rac)} &
\end{tikzcd}$$

From the data of Figures 1 and 2, the overall rate constants for disappearance of **5** and **6** at 152.0° can be obtained, namely $k_1 + k_3 = 1.30 \times 10^{-5}\ \text{sec}^{-1}$ and $k_4 + k_5 = 2.20 \times 10^{-5}\ \text{sec}^{-1}$ (±5% in each case). The ratio $k_1/k_3$ equals 0.475 from the first point at 10% reaction of **5**, but this is a minimum value since **6** reacts substantially faster than **9** and **10** or even **5**; therefore, this ratio was set equal to 0.55, not arbitrarily but to reproduce the found percentages of **6**, **9**, and **10** in the reaction of **5** (Figures 3–5). If $k_2$ is set equal to zero in the above expressions, then the per cent racemization of **5** calculated during the first 36% of reaction of **5** is less than that found by a factor of one-half. However, if $k_2$ is set equal to $0.13 \times 10^{-5}\ \text{sec}^{-1}$ or $^1/_{10}$th that of $k_1 + k_3$, then not only are the percentages of products reproduced but the per cent racemization of **5** is mimicked. The observation that $k_2$ be appreciable is unaltered even when $k_1 + k_3$ or $k_4 + k_5$ are varied by ±10% either separately or together. The only calculated points that do not correspond to the experimental values are the first and last ones (Figure 3). In the first the difference in rotation between starting material, **5**, and recovered **5** was at about the limit of detection and therefore suspect. In the last the rotation was taken on a relatively small sample of **5**. Further, the calculated per cent of racemization at the last point may be higher than what is actually the case since the kinetic scheme did not consider the subsequent reaction of racemic **5** to **6**, **9**, and **10**. This assumption breaks down as the extent of reaction increases. Thus, the curve that describes the calculated per cent racemization of **5** as a function of time (Figure 3) must rise faster with increasing reaction time than is actually the case at longer reaction times.

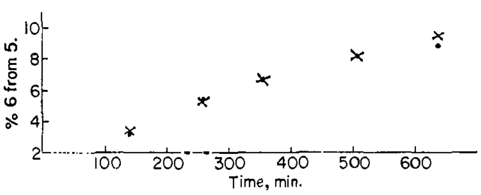


Figure 4. Per cent **6** from active **5** as a function of time at 152.0°: ×, experimental; ●, calcd with $k_2 = 0.13 \times 10^{-5}\ \text{sec}^{-1}$.

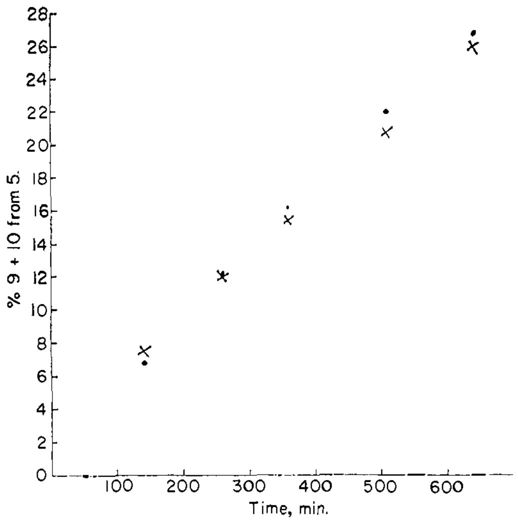
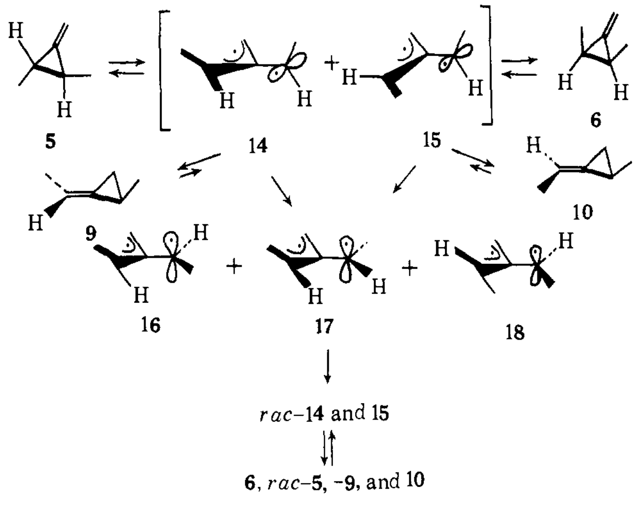


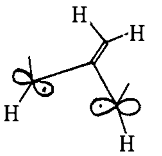
Figure 5. Per cent **9** + **10** from active **5** as a function of time at 152.0°: ×, experimental; ●, calcd with $k_2 = 0.13 \times 10^{-5}\ \text{sec}^{-1}$.

The requirement for a significant value for $k_2$ renders the previously developed scheme (above) for the methylenecyclopropane degenerate rearrangement incomplete since provision for this racemizing pathway must be made. Rather than involving an entirely separate pathway for racemization, we propose that another intermediate or transition state be added to the original scheme, this being the planar trimethylenemethane diradical. This species is attractive in that it can easily be formed by rotation about the bond joining the carbon bearing the orthogonal half-filled p orbital and the central carbon of the allyl radical in **14** and **15**. Three geometric isomers of the dimethyl planar diradical, namely **16**, **17**, and **18**, are possible. If these species are responsible for the excess racemization of **5**, then they should also produce excess racemization in the products

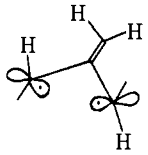


**9** and **10**, a possibility that can neither be demonstrated nor ruled out because of the large error limits on the optical purity of **9** produced in the rearrangement. Nonetheless, these achiral species are best regarded as transition states or intermediates for interconversion of **14** and **15** and their enantiomers and not as entities formed directly from **5** or **6** and independent of **14** or **15**. Indeed, on structural grounds it is difficult to envision formation of **16–18** without formation of **14** or **15**.

An alternative to planar trimethylenemethane diradicals for explanation of the excess racemization would be the bisorthogonal trimethylenemethane diradicals. With methyl substitution two such species could be envisioned, namely the cisoid and transoid forms **19** and **20**, respectively. The former is achiral while the latter is chiral, and both can be formed by rotation about the allyl radical portion. As previously noted, this requires loss of allyl radical resonance energy, and so these species would be expected to be 12.6 kcal/mol higher in energy than **14** or **15**. Whether or not these species then are accessible on the energy surface of this rearranging system is discussed below.



**19**



**20**

**Energy Surface for the Dimethylmethylenecyclopropane Interconversions.** The fact that the ratio of **9** to **10** is the same from both **5** and **6** suggests that the transition states or intermediates for formation of the orthogonal diradicals, **14** and **15**, are identical when derived from **5** or **6**. However, the transition state for formation of **6** from **5** must be 0.5 kcal/mol higher in energy than that for formation of **9** since the ratio of **9** to **6** is 2 when produced from **5** at 152.0°. By the same token, the transition state energy for formation of **5** from **6** must be the same as that for formation of **9** from **6**, all of this assuming that **14** and **15** partition themselves similarly. Therefore, the transition state for conversion of **6** to **14** must lie 0.5 kcal/mol higher in energy than that for formation of **14** from **5**. Consistent with this suggestion is the fact that the rate of formation of **5** and **9** from **6** is 1.6 times faster than the formation of **6** and **9** from **5** at 152°. This corresponds to a $\Delta\Delta F^{\ddagger}$ of 0.4 kcal/mol. Since the **5** to **6** ratio is 2.5 at equilibrium at 152°, corresponding to a free-energy difference of 0.8 kcal/mol, the transition state energy difference between that from **6** and that from **5** is 0.4 kcal/mol. Since there would appear to be little entropy difference between the transition states, the enthalpy differences are probably equivalent to the free-energy differences.

Unfortunately, there is no way to estimate the energy difference between **14** and **15** and the transition states forming them from this kinetic data. However, the heat of formation of the orthogonal dimethyltrimethylenemethane diradical like **14** relative to that of **5** or **6** can be approximated by an extension of Benson's arguments for the cyclopropane isomerizations.[10–12] Thus, the difference in enthalpy between **5** and **14** is 50 kcal/mol (the enthalpy difference between dimethylcyclopropane and the dimethyltrimethylene diradical[11]) − 13.5 kcal/mol (the incremental strain of the methylenecyclopropane system over cyclopropane and an isolated double bond[13]) − 12.6 kcal/mol (the allyl radical resonance energy[14]) = 23.9 kcal/mol. If the preexponential term for the rearrangement of **5** is similar to that for the methylmethylenecyclopropane, namely $10^{14.26}$, then the enthalpy of activation for conversion of **5** to **14** at 152° is roughly 36.3 kcal/mol. Thus, the enthalpy difference between **14** and the transition state leading to it is about 12.5 kcal/mol (36.3 − 23.9).

It was suggested previously[1] that **14** was more stable than **15** on the basis of the relative amounts of **9** and **10** that were formed. A stabilizing half-filled p-orbital–methyl interaction was suggested to account for this difference in stability. Whether or not such a destabilizing interaction exists, it is clear that in thermal ring openings of methylenecyclopropanes[2d,f] and cyclobutenes[15] bulky hydrocarbon residues and chlorine substituents tend to rotate outward, that is, away from the center of the ring in the precursor.

A final point concerns the relative stabilities of the achiral species in the rearrangements which were presumed to be the planar trimethylenemethane diradicals, **16–18**. Since the rate of excess racemization of **5** is one-tenth that for its conversion to **6**, **9**, and **10**, the transition state leading to **16–18** must be 2 kcal/mol higher in energy than that leading to **14**. As indicated above, if **16–18** are the achiral intermediates, they are best formed by a 90° rotation about the carbon bearing the orthogonal half-filled p orbital fused at the center of the allyl radical portion of **14** and **15**. During this rotation the overlap between the p orbital and the allyl radical increases without a discontinuity or change in sign until complete overlap is achieved. Thus, the energy of the system would be expected to rise or decrease to that of the planar species starting from the orthogonal ones, **14** and **15**. Since the orthogonal diradicals **14** and **15** are calculated to be much lower in energy than the transition state for formation of the planar ones **16–18**, there is the strong suggestion that the transition state for formation of **16–18** is, in fact, the planar species, **16–18**. If this is true, then the enthalpy difference between the orthogonal and planar diradicals, **14–15** and **16–18**, respectively, is about 14.5 kcal/mol assuming small entropy differences. This enthalpy difference is difficult to reconcile on steric grounds, although **16** and **17** could be destabilized by as much as 2 kcal/mol relative to **14–15**[1] by the presence of the methyl groups in the plane;[16] so electronic effects appear to be important.

---

(10) S. W. Benson, *J. Chem. Phys.*, 34, 521 (1960).

(11) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968).

(12) D. M. Golden and S. W. Benson, *Chem. Rev.*, 69, 125 (1969).

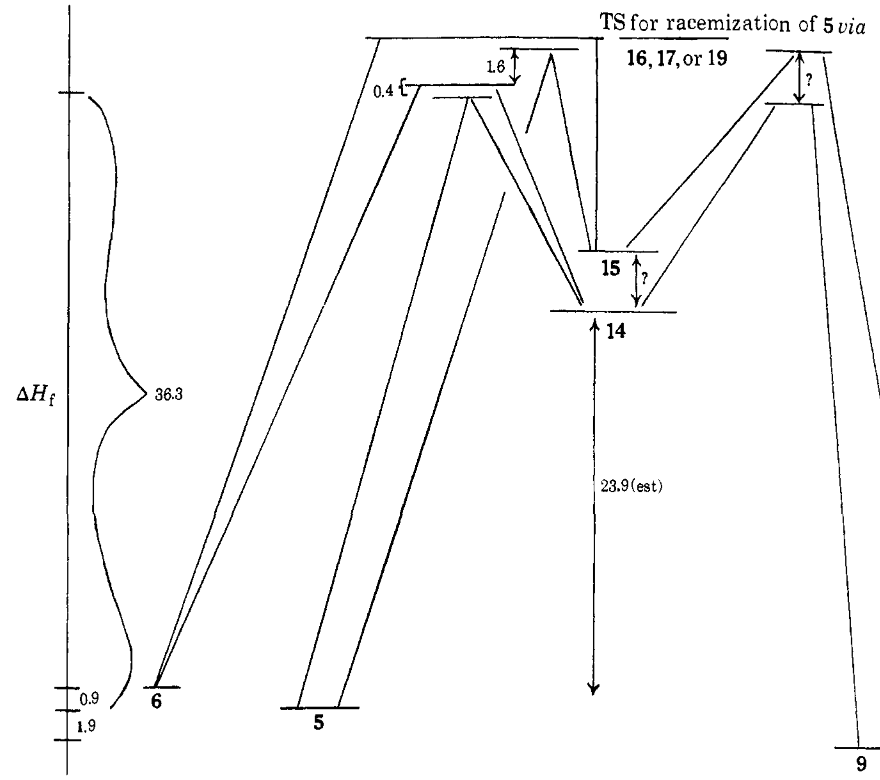
(13) (a) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, 90, 3395 (1968); (b) see also R. B. Turner, P. Goebel, B. J. Mallore, W. von E. Doering, J. F. Colburn, Jr., and M. Pomerantz, *ibid.*, 90, 4315 (1968).

(14) This assumes that there is no electrostatic interaction between the allyl radical and the half-filled orthogonal p orbital, a point which has neither experimental nor theoretical justification in this system.

(15) (a) H. M. Frey, *Trans. Faraday Soc.*, 60, 83 (1964); (b) R. Criegee, D. Seebach, R. E. Winter, B. Bovretzen, and H. A. Brune, *Chem. Ber.*, 98, 2339 (1965); (c) J. E. Baldwin and M. C. McDaniel, *J. Amer. Chem. Soc.*, 89, 1537 (1967).

(16) The planar *syn,syn*-dimethyltrimethylenemethane diradical (**18**) is probably substantially less stable than either **16** or **17** and therefore is probably not responsible for any of the racemization in the system. What is therefore important is the energy difference between **14** and **15** and **16** and **17**.

**Scheme I.** Possible Enthalpy Surface for the Dimethylmethylenecyclopropane Interconversions



As indicated above, the bisorthogonal species **19** and **20** may also be involved in the racemizing process, and **19** is, in fact, achiral. These species can reasonably be assumed to lie 12.6 kcal/mol higher in energy than **14** and **15** by virtue of loss of allyl radical resonance energy. Importantly, if **14** lies 12.5 kcal/mol lower in energy than the transition state forming it, then **19** and **20** are nearly isoenergetic with the transition state forming **14**, which means that they are 2 kcal/mol lower in energy than the transition state for excess racemization which was assumed to be the planar diradicals **16** and **17**. Thus, the excess racemization observed is due either to the planar and bisorthogonal diradicals **16**, **17**, and **19**, respectively, or simply to the intervention of **19** without formation of **16** and **17**. The implication then is that the planar trimethylenemethane diradical has no resonance energy or may, in fact, be conjugatively destabilized.[17]

An energy surface for the dimethylmethylenecyclopropane self-interconversions based on the above considerations is given below (Scheme I); however, it is important to remember that the enthalpies of the intermediates hinge on the calculated enthalpy difference between methylenecyclopropane and the orthogonal trimethylenemethane diradical. The scheme ignores any element of a concerted reaction, and as will be discussed below, the data do not rule out a concerted process, only the sole intervention of it. By the same token, the data do not require concert in the rearrangement.

**Relationship of the Dimethylmethylenecyclopropane Rearrangement to that of Feist's Ester and a Concerted Process.** The stereochemical results with the dimethylmethylenecyclopropane system are in marked contrast to those with Feist's ester studied by Ullman[2a] and later by Doering.[2g] In particular, geometric isomerization competes effectively with structural rearrangement in the former system but not in the latter one. Furthermore, trans starting material racemizes faster in the hydrocarbon case relative to the diester one. The mechanistic hypothesis developed above for the hydrocarbon system can easily be extended to the ester one if rearrangement to the $\alpha,\beta$-unsaturated compounds **2** and **3** is faster than reclosure of the diradicals **14** and **15** ($CH_3 = CO_2CH_3$) to *cis*- and *trans*-**1**. This is reasonable on electronic and steric grounds. Secondly, the fact that little racemization occurs with Feist's ester may be attributed to the instability of diradicals like **16**–**18** due to increased steric interactions of the carbomethoxy groups over those of methyl groups.

It is important to note that in none of the systems thus far investigated can there be any assessment of the extent of involvement of a concerted pathway for formation of the rearranged products. The data available with the hydrocarbon system **5**, **6**, **9**, and **10** do not require it, and indeed, the observation of geometric isomerization ($\mathbf{5} \rightleftarrows \mathbf{6}$) rules it out as the sole pathway unless this geometric isomerization involves an unprecedented pathway independent of the rearrangement studied.[18,19] There is, however, the possibility that the concerted pathway is a parallel one.

---

[17] R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

[18] The planar diradicals **16**–**18** could not be responsible for the geometric isomerization since the trans hydrocarbon **5** does not racemize as fast as **6** is produced from optically active **5**.

[19] It is conceivable that reversible homolytic cleavage of the 1,2-vinylic bond in **5** and **6** could be responsible for the geometric isomerization; however, it would appear to be energetically unfavorable. Using Chesick's[2b] and Doering's[2g] arguments, the activation energy for cleavage of any bond in methylenecyclopropane without any assistance of allyl radical resonance energy is 65 kcal/mol (the activation energy for cyclopropane cleavage) − 13.5 kcal/mol (the extra strain of methylenecyclopropane system) − 2.5 kcal/mol (the methyl stabilization in **5** or **6**) = 49 kcal/mol. This is at least 10 kcal/mol higher than the activation energy for the interconversion of **5** and **6**.

## Experimental Section

**General.** Nuclear magnetic resonance spectra were recorded on Varian A-60, HA-100, and HR-220 spectrometers. Carbon tetrachloride was used as a solvent with chloroform as an internal lock in frequency sweep mode; chemical shifts are reported as $\delta$ values in parts per million downfield from TMS. Infrared spectra were obtained with Perkin-Elmer Model 137 and 137G spectrophotometers in the indicated solvent. Vapor-phase chromatography was performed on Varian Aerograph A90P-3 and Series 1220-2 (capillary) instruments using the indicated columns. Mass spectra were taken on an AEI MS-9 mass spectrometer operating at 70 eV.

**Retention Times of 5, 6, 9, and 10 on Capillary Analytical Columns.** For the analyses of the hydrocarbons **5**, **6**, **9**, and **10**, two different capillary vpc columns were employed: one was a 200 ft × 0.01 in. i.d. didecyl phthalate (DDP); the other was a 200 ft × 0.01 in. i.d. di-*n*-butyl tetrachlorophthalate (DBTCP) column. The retention times on the DDP column operated at 60° and 10 psi helium pressure of **5**, **6**, **9**, and **10** were 17.3, 20.2, 20.9, and 21.2 min, respectively, with a width at half-height of 0.3 min at 20 min. The retention times of **5**, **6**, **9**, and **10** on the DBTCP column operated at 40° and 16 psi helium pressure were 16.6, 19.5, 19.9, and 20.4 min, respectively, with a width at half-height of 0.3 min at 20 min. These retention times and resolution measurements are given for the columns near the end of their useful life, as are those reported under Pyrolysis of 5, 6, and 9 in Sealed Tubes, part b, below.

**Racemic *trans*-2,3-Dimethylmethylenecyclopropane (5).** To 6.0 g (0.16 mol) of lithium aluminum hydride in 300 ml of diethyl ether was added 14.3 g (0.0844 mol) of Feist's acid dimethyl ester, **1**, at a rate to ensure gentle reflux. After heating at reflux for 1 hr, the reaction mixture was decomposed by slow addition of a freshly prepared saturated solution of anhydrous sodium sulfate. The ether layer was decanted and the salts were washed well with ether. The organic solutions were combined, dried over anhydrous sodium sulfate, and evaporated giving a colorless oil which was distilled at 0.7 Torr (bp 94–97°) giving 3.5 g of a clear colorless viscous oil which was *trans*-Feist's diol: nmr (60 MHz in CDCl$_3$) $\delta$ 1.63 (m, 2 H), 3.13 (d of d, $J$ = 12, 8 Hz, 2 H), 3.87 (d of d, $J$ = 12, 5 Hz, 2 H), 4.6 (broad singlet, 2 H), and 5.43 (t, $J$ = 2 Hz, 2 H). This material was combined with 0.5 g of material from another run [a total of 4.0 g (0.0350 mol)] and added to 14.3 g (0.075 mol) of recrystallized *p*-toluenesulfonyl chloride in 40 ml of pyridine at 0°. After stirring the reaction mixture at 0° for 3 hr, water was added which resulted in precipitation of a crystalline solid which was collected by filtration. A total of 9.5 g of material was obtained, 9.0 g of which was treated immediately with 6.5 g of sodium iodide in 400 ml of acetone. The clear reaction mixture was heated at reflux for 1 hr, and a white solid precipitated which was removed by filtration after the reaction mixture had cooled. Ether was added to the residue upon evaporation of the solvent. This solution was then washed with a solution of sodium sulfite until the organic layer was colorless. After drying over anhydrous sodium sulfate, the solution was evaporated under vacuum giving 6.5 g of a clear, light yellow, dense, viscous oil which was reduced immediately by addition of the neat liquid to a slurry of excess lithium aluminum hydride in diethoxydiethylene glycol at 90° at 100 Torr with 900 $\mu$l of the volatile product being trapped at 77°K. This material, *trans*-2,3-dimethylmethylenecyclopropane (**5**), was purified by vpc on a 20 ft × $^3/_8$ in. Carbowax 20M column operated at 40° and 50 ml/min flow with good recovery and found to be +99% pure by capillary vpc on a 200 ft didecyl phthalate column: nmr of **5** (100 MHz CCl$_4$) $\delta$ 1.0 (m, 2 H), 1.13 (asymmetric doublet with fine structure, 6 H), and 5.29 (t, $J$ = 2 Hz, 2 H); ir (CCl$_4$) 3020, etc., 1760 (w), 1740, 1450, 1375, 1150, 1065, 930, 885 (s) cm$^{-1}$; *m/e* 82.0782; calcd for C$_6$H$_{10}$, 82.0783.

***cis*-2,3-Dimethylmethylenecyclopropane (6).** In a manner similar to that described above for the reduction of Feist's ester, *cis*-Feist's acid anhydride (**8**) was reduced to *cis*-Feist's diol: nmr (CCl$_4$ at 100 MHz) $\delta$ 2.0 (m, 2 H), 3.31 (t with fine structure, $J$ = 10 Hz, 2 H), 3.90 (d of d, $J$ = 11, 5 Hz, 2 H), 4.75 (s, 2 H), and 5.38 (t, $J$ = 2 Hz, 2 H). This material was converted to the ditosylate, then to the diiodide, then to the hydrocarbon as described above. The hydrocarbon, *cis*-2,3-dimethylmethylenecyclopropane (**6**), was purified with good recovery as described above for **5** and found to be +99% pure by capillary vpc on a 200 ft didecyl phthalate column: nmr of **6** (100 MHz, CCl$_4$) $\delta$ 1.09 (asymmetric doublet with fine structure, 6 H), 1.45 (m, 2 H), and 5.25 (t, $J$ = 2 Hz, 2 H); ir (CCl$_4$) 3025, etc., 1780 (w), 1740 (w), 1450, 1440, 1370, 1150, 1125, 1080, 990, 940, and 890 (s) cm$^{-1}$; *m/e* 82.0770.

**Resolution of Feist's Acid.** To 32 g of Feist's acid dissolved in a minimum volume of boiling ethanol was added 89 g of brucine dissolved in a minimum volume of boiling ethanol; then enough water was added to make a 3:1 ethanol–water mixture. Upon cooling, 75 g of a light brown powder was obtained which was recrystallized once from a 3:1 ethanol–water mixture. Obtained were a head crop of crystals, 46 g, and a second crop, 13 g. Regeneration of the acid from each portion of these by treatment with acid and extraction with ether followed by optical measurements gave $[\alpha]^{22}\text{D}$ −149.6° (*c* 1.275, EtOH) for the head crop and $[\alpha]^{22}\text{D}$ −136° for the second crop. A second recrystallization of the head crop resulted in Feist's acid with $[\alpha]^{22}\text{D}$ −147.0° (EtOH). Combination of head crops of subsequent recrystallizations of the second crop with the initial head crop gave 45 g of the salt which was treated with dilute hydrochloric acid in the presence of ether. Extensive extraction of the aqueous layer after saturation with sodium chloride followed by drying and evaporation of the solvent gave 5.0 g of Feist's acid: $[\alpha]^{22}\text{D}$ −149.4° (*c* 1.45, EtOH).[20]

**Optically Active *trans*-2,3-Dimethylmethylenecyclopropane (5a).** To 2.57 g (0.066 mol) of lithium aluminum hydride in 150 ml of diethyl ether was added 5.6 g (0.0329 mol) of optically active Feist's acid, dimethyl ester ($[\alpha]^{22}\text{D}$ of acid −149.4° (EtOH)), dropwise with stirring. After addition was complete, the reaction mixture was heated at reflux for 10 min and then decomposed with a freshly prepared saturated solution of anhydrous sodium sulfate. The ethereal solution was decanted from the precipitated salts; then the salts were washed well with tetrahydrofuran. The washings and original ether solution were combined and were dried over anhydrous sodium sulfate. After evaporation of the solvent under aspirator vacuum, a colorless viscous oil was obtained which was distilled bulb to bulb at 0.7 Torr giving 3.37 g (91%) of Feist's diol; 3.25 g (0.029 mol) of this diol was added to 13.3 g (0.07 mol) of recrystallized *p*-toluenesulfonyl chloride in 50 ml of pyridine at 0° followed by stirring at 0° for 3.5 hr and followed by addition of water and extraction with ether. The ether layer was washed with cold, dilute hydrochloric acid solution until the washings were acidic, then the ether layer was washed successively with water, 10% sodium bicarbonate solution, and with saturated brine. After drying over anhydrous sodium sulfate and evaporation of the solvent, 11.0 g of crude ditosylate was obtained which was immediately treated with 11.0 g (0.069 mol) of sodium iodide dissolved in 130 ml of acetone. After heating at reflux for 45 min, the mixture was filtered, the solvent was evaporated, and the ether was added. The ethereal solution was washed with a saturated sodium sulfite solution until the organic layer was colorless. After drying over anhydrous sodium sulfate, the solvent was evaporated giving 8.10 g of Feist's diiodide. Conversion of the diiodide to **5a** involved addition of 3.15 g of the diiodide to excess lithium aluminum hydride in diethoxydiethylene glycol at 90° and 100 Torr with the volatile material being collected in a trap cooled by liquid nitrogen; 770 $\mu$l of material was obtained which had a small amount of diethyl ether present. Purification of the hydrocarbon by passage through a 15 ft × $^1/_4$ in. dibutyl tetrachlorophthalate (DBTCP) column operated at 55° and 35 ml/min flow rate twice gave **5a**, $[\alpha]^{22}\text{D}$ −57.5° (CCl$_4$). Repassage of this material through a 5 ft × $^1/_4$ in. SE-30 column gave **5a**, $[\alpha]^{22}\text{D}$ −57.6° (*c* 1.72, CCl$_4$). Analysis on a 200-ft DBTCP capillary column revealed that **5a** was +99% pure. The nmr of this material was identical with that of **5r**. A sample of **5** prepared from the same batch of the diiodide had $[\alpha]^{22}\text{D}$ −59.4° (*c* 1.468, CCl$_4$) after purification only through a SE-30 vpc column.

***anti*-2-Methylethylidenecyclopropane (9).** *anti*-2-Ethylidene-1-carbethoxycyclopropane[7] was converted to *anti*-2-methylethylidenecyclopropane (**9**) by the same reductive sequence described above for the conversion of Feist's ester to **5**. The hydrocarbon was purified by preparative vpc on either a $^1/_4$ in × 18 ft SE-30 column at 30° and 40 ml min flow or a $^1/_4$ in. × 15 ft DBTCP column at 45° and 35 ml/min flow: nmr (100 MHz) of **9** (CCl$_4$) $\delta$ 0.65 (broad singlet, 1 H), 1.21 (singlet with fine structure, 4 H), 1.38 (broad singlet, 1 H), 1.82 (doublet with fine structure, $J$ = 5.5 Hz, 3 H), and 5.77 (m, 1 H); ir (CCl$_4$) 3000, etc., 1440, 1415, 1370, 1300, 1150, 1090, 1060, 1020, 980 sh, 965, 950 and 875 cm$^{-1}$; *m/e* 82.0784.

***syn*-2-Methylethylidenecyclopropane (10).** *syn*-2-Ethylidene-1-carbethoxypropane[7] was converted to *syn*-2-methylethylidene-

---

(20) The low recovery here suggests that the head crop was actually the bisbrucine salt of Feist's acid.

Table I

| | | Yield, % | | | |
|---|---|---|---|---|---|
| | | **5** | **6** | **9** | **10** |
| Temp, °C | Time, min | Retention time, min | | | |
| | | 15.3 | 19.5 | 20.9 | 21.1 |
| 255 | 60 | 6.5 | 3.7 | ~45 | ~45 |
| 230 | 90 | 6.8 | 3.4 | ~44.9 | ~44.9 |
| 190 | 80 | 14.6 | 5.5 | ~66 | ~13 |

Table II

| Starting material | Time, sec | % **5** | % **6** | % **9** | % **10** | $k$ |
|---|---|---|---|---|---|---|
| **5** | 1320 | 89.1 | 3.6 | 7.3 ± 0.3 | 1.2 ± 0.3 | $0.83 \times 10^{-5}$ sec$^{-1}$ |
| **5** | 7200 | 56.6 | 10.8 | 28.1 ± 1 | 4.5 ± 1 | |
| **6** | 1320 | 9.4 | 82.0 | 8.3 ± 0.3 | 1.3 ± 0.3 | $1.36 \times 10^{-5}$ sec$^{-1}$ |
| **6** | 4680 | 54.0 | 27.8 | 15.9 ± 0.6 | 2.6 ± 0.6 | |

Table III

| Time, sec | % **5** | $[\alpha]^{22}\mathrm{D}$, ° | % rac | % **6** | % **9** | $[\alpha]^{22}\mathrm{D}$, ° | % **10** |
|---|---|---|---|---|---|---|---|
| 720 | 86.0 | −58.6 | 1.4 | 4.6 | 7.5 ± 0.4 | +13.6 | 1.7 ± 0.4 |
| 1800 | 62.3 | −55.0 | 7.4 | 9.8 | 23.3 ± 1.0 | +12.8 | 4.0 ± 1.0 |
| 4800 | 44.7 | −45.1 | 24.1 | 11.4 | 37.7 ± 1.5 | +11.75 | 6.3 ± 1.5 |

cyclopropane (**10**) by the same reductive sequence described above for the conversion of Feist's ester to **5**. The hydrocarbon was purified as described above for purification of **9**: nmr (100 MHz) of **10** ($CCl_4$) $\delta$ 0.68 (broad singlet, 1 H), 1.20 (unsymmetrical doublet, $J$ = 5 Hz, 3 H), 1.35 (broad multiplet as a shoulder, 2 H), 1.82 (d of q, $J$ = 6.5, 2.0 Hz, 3 H), and 5.68 (broadened quartet, $J$ = 6.5 Hz, 1 H); ir ($CCl_4$) 3000, etc., 1450, 1365, 1145 (w), 1105, 1060, 1015, 970, 920, and 875 cm$^{-1}$; $m/e$ 82.0775.

**Pyrolysis of 5, 6, and 9 in Sealed Tubes. a. General Procedure.** Open-end Pyrex tubes of volumes ranging between 5 and 200 ml were washed with acetone and then water and rinsed with dilute ammonium hydroxide solution. After drying the tubes in an oven at 95°, samples of the hydrocarbon in open-end capillaries were dropped in, and the tubes were attached to a vacuum system. After cooling, in liquid nitrogen, the tubes were evacuated to 0.5 Torr and sealed with a torch. The tubes were then placed in an appropriate oven at the stated temperature. After heating for the requisite time, the small ends of the tubes were cooled in liquid nitrogen, broken open, and analyzed as indicated.

**b. Equilibration Studies.** Samples of **5** were heated at 255, 230, and 190° in a crudely thermostated air oven for 60, 90, and 80 min, respectively. The analyses on a 200-ft didecyl phthalate capillary column at 33° and 10 psi are given in Table I. The combined values for **9** and **10** are accurate; however, the relative amounts are uncertain because the width at half-height for peaks with that retention time was 0.3 min. A sample of **6** was heated at 150° for 75.5 hr giving 9.7% of **5**, 3.5% of **6**, 64.8 ± 5% of **9**, and 22 ± 5% of **10**. Finally, a sample of **5** was heated at 240° for 4 hr, then at 150° for 1 week, giving 6.25% of **5**, 2.5% of **6**, 47.8% of **9**, and 43.8% of **10**.

**c. Kinetic Runs at 169°.** In each of two 4-ml tubes was sealed in 4 $\mu$l of **5**, and in each of two 4-ml tubes was sealed in 4 $\mu$l of **6**. These four tubes were reheated to 100° in an air oven, then placed in an oil bath at 169 ± 1° thermostated with a thermowatch device. After the indicated times, the tubes were removed and analyzed on the 200-ft DDP capillary column (Table II).

**d. Pyrolysis of Optically Active 5 at 170°.** In each of three 100-ml tubes was sealed in 85–200 $\mu$l of optically active **5**, $[\alpha]^{22}\mathrm{D}$ −59.4° ($CCl_4$). These tubes were heated in an air oven at approximately 170°. After the indicated times, the contents of the tubes were analyzed and separated by vpc on a 6 ft × $^3/_4$ in SE-30 column operated at room temperature and 20 ml/min flow. In this way very pure **5** by capillary vpc was recovered and its identity was confimred by nmr. The mixture of **6**, **9**, and **10** was obtained, analyzed by capillary vpc, and also confirmed by nmr. Rotations of these samples were taken and the rotation of **9** and **10** was corrected for the amount of **6** present (Table III).

**Pyrolysis of Optically Active 5 and 6 in a Conditioned Static Reactor. a. Apparatus.** In a well-insulated cabinet was placed a 10-l. stainless steel beaker containing a 1:1 mixture of potassium nitrate and sodium nitrate. The mixture was heated with a 500-W base heater controlled by a Variac, and fine temperature control was achieved with a 125-W heater driven by a Bailey Controller Model 76-8 which was actuated by a platinum resistance thermometer. Stirring was provided by a "Lightening" stirrer. Temperature readout throughout the solution was provided by three matched copper-constantan thermocouples. In the bath was suspended 2-l., 200-ml, and 50-ml reactors each with a 2-mm i.d. capillary tube leading to a Teflon stopcock 30 cm above the surface of the liquid. The other exit of the stopcock was attached to a vacuum line which was evacuated by an oil diffusion pump. All of the capillary tubing was wrapped with heating tape controlled by Variacs, and temperatures were monitored by thermocouples. All the kinetic runs with **5** and **6** were conducted in the 200-ml reactor which had been used previously for innumerable hydrocarbon thermolyses. The temperature variation across this vessel and between all the runs reported here was ±0.1°.

**b. Pyrolysis of Optically Active 5.** Into the 200-ml reactor at 152.0° was expanded 100 $\mu$l of optically active **5**, $[\alpha]^{22}\mathrm{D}$ −57.5°. After a given time the material was removed, collected from the vacuum line, analyzed on a 200 ft DDP capillary column, and then separated on an SE-30 column as described above in the sealed tube reactions. The data are plotted in Figures 1 and 2.

**c. Pyrolysis of 6.** Into the 200-ml reactor at 152.0° was expanded 10 $\mu$l of **6**. After a given time the material was removed, collected from the vacuum line, and analyzed on the 200 ft DDP capillary column. The data are given in Figure 1.

**Conversion of Optically Active 9 to *cis*-1-Ethyl-2-methylcyclopropane (13).** The samples of **6**, **9**, and **10** collected from each of the kinetic runs with optically active **5** at 152.0° were combined (0.0302 g) and found to have $[\alpha]^{22}\mathrm{D}$ +12.0° ($c$ 3.05, $CCl_4$) corrected for 21.7% of **6** present and 6.9% of **5** whose rotation was estimated to be −55°. This mixture was carefully separated on a 15 ft × $^1/_4$ in. di-$n$-butyl tetrachlorophthalate (DBTCP) column operated at 70° and a flow rate of 25 ml/min. Obtained was 0.0116 g of material consisting of **6** (26%), **9** (72%), and **10** (2%), $[\alpha]^{22}\mathrm{D}$ +10.7° ($c$ 1.17, $CCl_4$) after correction for the presence of **6**.

The solution used for rotation (0.99 ml) was hydrogenated over platinum at atmospheric pressure. Vpc analysis of the mixture on a DBTCP capillary column indicated the presence of seven peaks in the percentages 25.2:1.5:7.8:7.8:4.32.2:20.6 with the first three major peaks being the $C_6H_{14}$ hydrocarbons. The 32.2% peak was *cis*-1-ethyl-2-methylcyclopropane (**13**) by comparison of vpc retention times and nmr with an authentic sample, and the 20.6% peak was *cis,cis*-1,2,3-trimethylcyclopropane (nmr ($CCl_4$ at 220 MHz) $\delta$ 0.7 (m, 3 H) and 0.85 (m, 9 H)). This mixture was rehydrogenated but the product distribution was unchanged. To this solution was added 60 $\mu$l of carbon tetrachloride giving a total of 750 $\mu$l; assuming that the hydrocarbons and solvent have the same volatility, the concentration of this solution was 0.0108 g/ml, and it had an observed rotation of −0.035° corresponding to an $[\alpha]^{22}\mathrm{D}$ − 10.0 ± 1.5° ($CCl_4$) of **13** if it were the only chiral species present. This mixture was separated on a 15 ft × $^1/_4$ in DBTCP column at 50° and 50 ml/min flow giving pure **13** which was immediately dissolved in 0.99 ml of isooctane, and 2.0 μl of cyclohexane was added. Vpc analysis on DBTCP revealed a 2:1 ratio of cyclohexane and **13**. The observed rotation of this solution was −0.010°. Assuming the density of **13** to be the same as that of cyclohexane, the $[\alpha]^{22}\mathrm{D}$ was −12.8° (isooctane) for **13**.

**Acknowledgment.** I thank the donors of the Petroleum Research Fund, administered by the American Chemical Society (2754-A1,4), for partial support of this work and Mr. L. T. Burka and Mr. W. A. Black for valuable assistance with some of the experiments and building the vapor-phase kinetics bath. Acknowledgment is also made to the National Science Foundation for funds for the purchase of the mass spectrometer used in this work (Grant No. GP-5234).

# The Mechanism of Photoisomerization of 3,5-Heptadienone[1]

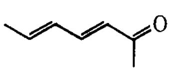
**Arthur F. Kluge[2a] and C. Peter Lillya[2b]**

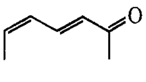
*Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002. Received July 1, 1970*

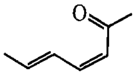
**Abstract:** Irradiation of 3,5-heptadienone in dilute diethyl ether solution interconverted the trans,trans, the cis,trans, and the trans,cis isomers in a clean reaction. The products of triplet sensitized isomerization were the same. Variation of sensitizer triplet energy leads to the conclusion that the lowest dienone triplet lies at *ca.* 54 kcal/mol. Azulene did not quench the isomerizations and the quantum yields for direct isomerization do not account for the photostationary state observed in the presence of high-energy sensitizers ($E_T > 58$ kcal/mol). The wavelength dependent quantum yields show that isomerization does not proceed exclusively *via* a common excited state or *via* isomeric excited states which equilibrate faster than they decay.

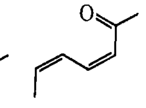
Photochemical cis–trans isomerization has proved a fertile field for mechanistic organic photochemistry. Simple on the surface, these reactions have proved unusually rich in mechanistic detail and subtlety. Photoisomerization of stilbene is a good example. Hammond and his coworkers invoked the intermediacy of a "phantom triplet" in the sensitized isomerization[3] and also developed a method for examining nonvertical transfer of energy from sensitizers to substrate.[4] Some controversy still exists about whether direct photoisomerization of stilbene proceeds *via* singlet[5] or triplet[6] intermediates. Recently, 2,4-hexadiene, which has two isomerizable double bonds in conjugation, has been studied. Direct irradiation produces the three geometric isomers,[7] and detailed studies show that the excited singlet states derived from geometrically isomeric ground states do not equilibrate with one another.[8] Data for sensitized isomerization of 2,4-hexadiene are consistent with a mechanism involving a common triplet or rapidly interconverting isomeric triplets.[9,10]

Our interest in photoisomerization of conjugated dienones led us to investigate mechanistic details in the case of 3,5-heptadienone. Photoisomerization of this dienone is typical of that of a number of these compounds which we have studied.[11] Irradiation of any of the three known geometric isomers (tt, tc, and ct) as a $10^{-2}$–$10^{-3}$ *M* solution in ethyl ether gives, in high yield, the same photostationary mixture of these three isomers.

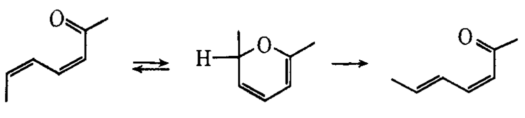

tt


tc


ct


cc

Isomerization is by far the most efficient photoreaction of these dienones. In fact under our conditions no other volatile products can be detected. As is the case for all 14 dienones we have studied, irradiation of 3,5-heptadienones appears to give none of the cis,cis isomer (cc).[12] It seems likely that the absence of cc is caused not by its lack of formation but rather by its subsequent conversion to ct in a dark reaction (eq 1).[11]


(1)

**Spectroscopic Studies.** The 3,5-heptadienone isomers exhibit both n → π* and π → π* absorption maxima in diethyl either solution.[13] The lowest excited singlet state has an nπ* configuration and an

---

[1] Preliminary communication: A. F. Kluge and C. P. Lillya, *J. Amer. Chem. Soc.*, **92**, 4480 (1970).

[2] (a) N. S. F. trainee, 1965–1969; (b) Alfred P. Sloan Foundation fellow, 1969–1971.

[3] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

[4] W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

[5] (a) J. Saltiel, E. D. Megarity, and K. G. Kneipp, *ibid.*, **88**, 2386 (1966); (b) J. Saltiel, *ibid.*, **89**, 1036 (1967); (c) J. Saltiel, *ibid.*, **90**, 6394 (1968); (d) J. Saltiel, O. C. Zafiriou, E. D. Megarity, and A. A. Lamola, *ibid.*, **90**, 4759 (1968); (e) J. Saltiel and E. D. Megarity, *ibid.*, **91**, 1265 (1969).

[6] (a) K. Muszkat, O. Gegiou, and E. Fischer, *ibid.*, **89**, 4814 (1967); (b) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 12, 3907 (1968).

[7] R. Srinivasan, *ibid.*, **90**, 4498 (1968).

[8] J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970). This is also true of the excited singlets from *cis*- and *trans*-1,3-pentadiene: R. Srinivasan, *ibid.*, **92**, 3226 (1970).

[9] H. L. Hyndman, B. M. Monroe, and G. S. Hammond, *ibid.*, **91**, 2852 (1969).

[10] J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969).

[11] A. F. Kluge and C. P. Lillya, *J. Org. Chem.*, **36**, 1988 (1971).

[12] Examination of crude photolysates by ir, nmr, glpc, and tlc has failed to produce any evidence for the existence of *cis,cis*-dienones in these mixtures.

[13] A. F. Kluge and C. P. Lillya, *J. Org. Chem.*, **36**, 1977 (1971).