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# The Racemization of *trans*-1,2-Divinylcyclopropane

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The synthesis of (−)-*trans*-1,2-divinylcyclopropane and the kinetics of its racemization and conversion to 1,4-cycloheptadiene, presumably through *cis*-1,2-divinylcyclopropane, are described. It is concluded that the ring opening is not an electrocyclic process.

La synthèse du (−)-*trans*-divinyl-1,2 cyclopropane ainsi que la cinétique de sa racémisation et transformation en cycloheptadiène-1,4, probablement via le *cis*-divinyl-1,2 cyclopropane, sont rapportées. Il en a été déduit que l'ouverture du cycle n'est pas un processus électrocyclique.

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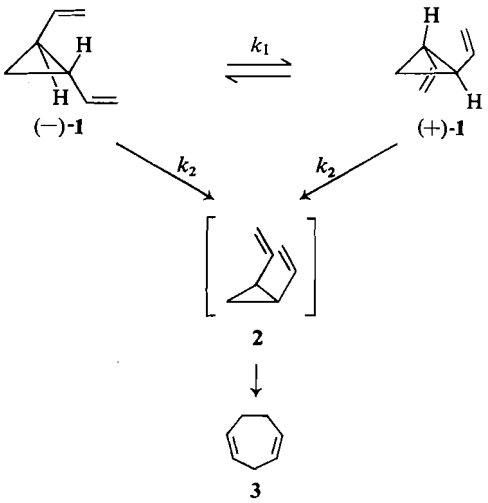
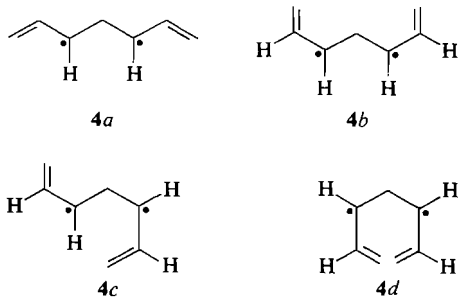
## Introduction

In attempting to discern whether the *O,O*-trimethylene species (1) is an important intermediate for the isomerization of cyclopropane we have examined the racemization of (*1S:2S*)-*trans*-1,2-divinylcyclopropane (**1**). This compound offers the advantage that the reactivity in thermal processes is primarily confined to the cyclopropane bond situated between the two vinyl groups. While there are numerous possible configurations for diradicals (2) we shall consider two measurable manifestations of diradical formation from **1**; (*a*) racemization and (*b*) geometrical isomerization. Geometrical isomerization of **1** leads to *cis*-1,2-divinylcyclopropane (**2**) which isomerizes rapidly and quantitatively to 1,4-cycloheptadiene (**3**). If there is a preferred mode of ring opening and closing, either dis- or conrotatory, then the rate of racemization should exceed the rate of formation of **3** by more than that expected from steric factors alone. Thus kinetically we would predict that for Scheme 1, $2k_1 > k_2$ (where $k_{rac} = 2k_1$). There remains the possibility of the formation of **3** directly from **1** via either a concerted or diradical process. The former seems unlikely in that *trans-trans*-1,4-cycloheptadiene would result from that conformation in which the termini of the vinyl groups are closest in **1**. There are ten possible *O,O*-trimethylene species resulting from dis- and




SCHEME 1

conrotatory ring opening of **1**; of these, **4***b*, *c*, and *d* have the requisite configurations such that rotation about a single bond (=CH—$CH_2$—) will generate the product **3**. Of these, **4***c* and *d* seem unlikely in that the alkyl group has moved inwards, a process known to be unfavorable from the racemization of oxiranes (3). The form **4***b* remains and the consequence of this, and the others if they still pertain, is to overemphasize $k_2$ and reduce the severity of this test for the *O*,*O*-trimethylene species.



**4***a* **4***b* **4***c* **4***d*

*Synthesis and Absolute Configuration of* **1**

Optically active **1** was prepared by resolving the known *trans*-2-vinylcyclopropanecarboxylic acid via its quinine salt. The resolved acid was then converted to *trans*-1,2-divinylcyclopropane as indicated in Scheme 2. The absolute configuration and optical purity of **1** was ascertained by oxidation to *trans*-1,2-cyclopropanedicarboxylic acid. Thus (*1S:2S*)-*trans*-1,2-divinylcyclopropane of 14% optical purity has a rotation $[\alpha]_{365}^{25}$ −40.2° (*c* 3.70, isopropyl alcohol).

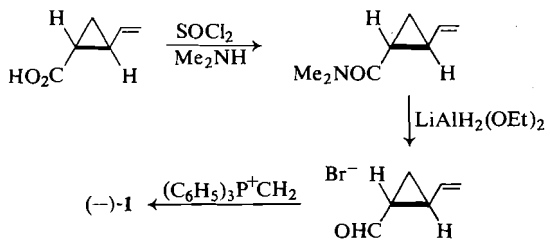
## Experimental

*(−)-trans-2-Vinylcyclopropanecarboxylic Acid*

The method of Vogel *et al.* (4) was used for the preparation of ethyl *cis*- and *trans*-2-vinylcyclopropanecarboxylate from ethyl diazoacetate and butadiene. The *cis* isomer was converted to the *trans* by refluxing the ester (50 g, 0.36 mol) with sodium ethoxide (made by adding 1.0 g of sodium metal to 100 ml absolute ethanol) in ethanol for 60 h. After saponification the acid was then partially resolved via its quinine salt by recrystallization from water. The acid, b.p. 82–83°/2–3 Torr gave $[\alpha]_D^{25}$ −60.0° (*c* 1.49, acetone).

*N,N-Dimethyl-trans-2-vinylcyclopropanecarboxamide*

*trans*-2-Vinylcyclopropanecarboxylic acid (28.1 g, 0.25 mol) was added slowly with stirring to freshly distilled thionyl chloride (140 g, 1.0 mol) and dry benzene (15 ml). The solution was maintained at 80° for 3 h and the excess thionyl chloride and benzene was distilled off. The remaining acid chloride was slowly added with stirring to a 25% solution of dimethylamine (180 g). The resulting amide was extracted with ether, washed with water and dilute sulfuric acid, and then dried over anhydrous sodium carbonate. After filtration the ether was removed and the amide distilled, b.p. 79–80°/2.5 Torr; yield 27.7 g, 80%.




SCHEME 2

*trans-2-Vinylcyclopropanecarboxaldehyde*

The aldehyde was prepared utilizing lithium diethoxyaluminohydride by the procedure of Brown and Shoaf (5). Ethyl acetate (9.7 g, 0.11 mol) was added slowly to a solution of lithium aluminum hydride (4.2 g, 0.11 mol) in 100 ml of dry ether. The resulting solution was transferred over a period of 30 min to a stirred solution of *N,N*-dimethyl-*trans*-2-vinylcyclopropanecarboxamide (27.2 g, 0.2 mol) in 40 ml of dry ether at 0°. The reaction mixture was stirred for an additional hour and then decomposed, with cooling, by adding to a 10% solution of sulfuric acid. The ether layer was washed, then dried over anhydrous sodium carbonate. The aldehyde distilled at 57.8°/30 Torr; yield 10.6 g, 58%.

*trans-1,2-Divinylcyclopropane (1)*

A solution of *trans*-2-vinylcyclopropanecarboxaldehyde (10 g, 0.11 mol) in 20 ml ether was added, under nitrogen, to a solution of methylenetriphenylphosphorene, which had been prepared by the addition of methyltriphenylphosphonium bromide (105 g, 0.28 mol) to butyl lithium (0.2 mol) in 100 ml of ether. The resulting complex was refluxed with 100 ml of tetrahydrofuran for 1 h and then the ether soluble portion, after addition to water, was carefully fractionated. The crude product was subjected to preparative gas chromatography using a 10 ft × 3/8 in., β,β′-oxydipropionitrile column operated at 35°. The n.m.r. and i.r. spectra correspond to those described in the literature (3), yield 50%, $[\alpha]_{365}^{25}$ −40.2° (*c* 3.70, isopropyl alcohol).

*Oxidation of (−)-1 to (1R:2R)-(−)-trans-1,2-Cyclopropanedicarboxylic Acid*

(−)-*trans*-1,2-Divinylcyclopropane (0.47 g, 5 mmol) was added to a 500 ml solution of sodium metaperiodate (15.05 g, 3 mmol) potassium permanganate (0.20 g, 1.2 mmol) in water (6). The reaction mixture was stirred at room temperature for 20 h and then acidified with 10% sulfuric acid. Ether extraction followed by drying and evaporation gave 0.31 g of a solid which upon recrystallization from water gave needles, m.p. 174–175° (lit. value 175° (7)) $[\alpha]_D^{25}$ −34.5° (*c* 2.26, water). The optical purity is thus 14% based on −247° and the absolute configuration is *1R:2R* (8). Thus the absolute configuration of (−)-**1** is *1S:2S*.

*Kinetic Measurements*

Samples of (−)-**1** (*ca.* 37 mg) were placed in break-seals of 20 ml volume, degassed, sealed, and placed in an air-bath

TABLE 1. Rate data, at 169.98°, for the conversion of **1** to **3** and the simultaneous racemization of (−)-**1**

| $t$ (s) | $-\log \alpha/\alpha_0$ | $-\log a/a_0$ | $10^5 k_1$ ($s^{-1}$) | $10^4 k_2$ ($s^{-1}$) |
|---|---|---|---|---|
| 1200 | 0.117 | 0.074 | 4.12 | 1.42 |
| 2400 | 0.263 | 0.150 | 5.42 | 1.44 |
| 3600 | 0.403 | 0.243 | 5.11 | 1.55 |
| 5400 | 0.630 | 0.372 | 5.50 | 1.58 |
| 7200 | 0.903 | 0.482 | 6.73 | 1.54 |
| ∞ | $\alpha = 0.00$ | $a = 0.00$ | | |
| | | | Average 5.38 (0.9)* | 1.51 (0.07)* |

*Standard deviation.

TABLE 2. Rate constants and activation parameters for Scheme 1

| Temperature ±0.03° | $10^6 k_1$ ($s^{-1}$) | $10^6 k_2$ ($s^{-1}$) | Activation parameter |
|---|---|---|---|
| 150.03 | 8.85±0.35 | 24.5±0.8 | $E_a^1 = 33 \pm 2$ kcal $mol^{-1}$ |
| 160.01 | 22.6 ±0.9 | 61 ±2 | $\log A^1 = 12.1$ |
| 169.98 | 54 ±6 | 151 ±5 | $E_a^2 = 34.3 \pm 0.9$ kcal $mol^{-1}$ |
| | | | $\log A^2 = 13.1$ |

controlled to ±0.03°. The tubes were removed at the appropriate times and quenched in an ice-water bath. The sample was then re-attached to the vacuum line and after a pressure of 10 μ was attained in the manifold the break-seal was opened and the contents transferred to a pre-weighed 1 ml volumetric flask that had been attached to the vacuum line by means of a finely ground 7/16 ⅋ male joint. The stoppered flask was then reweighed and isopropyl alcohol was added up to the 1 ml line. The total solution was weighed and the specific rotation $[\alpha]_t$ at time $t$ was calculated using the expression (9):

$$[\alpha] = \frac{100\alpha}{lpp_s}$$

where $\alpha$ is the observed angle, $l$ is the length of the polarimeter tube in dm, $p$ the concentration of product in g/100 g of solution, and $p_s$ the density of the solution. The density of the solution was not measured as it cancels in the kinetic expression. The rotations were measured using a thermostated polarimeter cell in a Perkin–Elmer 141 Polarimeter set at 365 nm. Infinity tubes were left to greater than ten half-lives and displayed no rotation. A sample corresponding to $t = 0$ was subjected to all of the manipulations except heating. No residual material was observed in any of the break-seals and a sample run using cyclohexane as a standard indicated that the transfer was greater than 95% efficient.

After measuring the rotation the solutions were analyzed by g.c. on a Varian Aerograph 1200 using a 10 ft column of SF-96 on Chromasorb-W. The peaks corresponding to **1** and **3** were integrated using a planimeter. No additional peak other than that of solvent was observed. An example run at 169.98° is given in Table 1. The rate constants were calculated on a point by point basis and the value for $k_1$ was obtained by using the expression: $k_1 = 2.303/2t(\log a/a_0 - \log \alpha/\alpha_0)$, where $a$ is the fraction of *trans*-1,2-divinylcyclopropane at time $t$.

## Results and Discussion

The rate constants for the interconversion of enantiomers, $k_1$, and for those assumed to be representative of the *trans* to *cis* isomerization, $k_2$, are listed in Table 2 along with their probable errors (10) and activation parameters. The precision in determining $k_1$ is poor since both the errors from the gas chromatographic assessment of the geometrical isomerization and the polarimetric errors for the racemization process are incorporated. The differences between the activation parameters for the two processes cannot be considered to be significant.

Operationally if the racemization is an electrocyclic process and only one mode of rotation (either con- or disrotatory) to the intermediate diradical, **4***a* being the most probable structure, is preferred, then the rate constant for the geometrical isomerization will be infinitely smaller than the rate constant for the racemization process. If however both con- and disrotatory modes are equally accessible, then, invoking the principle of microscopic reversibility, we can state that the racemization rate constant will be twice that of the rate constant

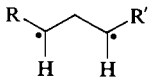
TABLE 3. Operative criteria

| Path | Predicted $k_2/k_1$ |
|---|---|
| Only one mode | 0 |
| Equivalent dis- and conrotation | 2 |
| Smith mechanism | ∞ |

for the geometrical isomerization.[1] If only one chiral center of the reactant (−)-**1** is rotated through 180° (the Smith mechanism (11)) then the starting material is not racemized but is only converted to **3**. This is summarized in Table 3.

The $k_2/k_1$ ratio observed at 160° for **1** is 2.8. The kinetic data indicate that within the assumptions made in the introduction, the more random diradical process is favored over that wherein only one mode of ring opening and closure is operative.

A problem arises in just what one might expect of a diradical that is free to close to either *cis*- or *trans*-1,2-divinylcyclopropane. If we are to use the definition of Hayes and Siu (12) then from the diradical we are equally likely to get closure to the *cis*-isomer as to the *trans*. This does not take into account the relative thermodynamic stabilities of the *cis*- and *trans*-isomers. If we assume that our diradical has a structure such as **5** where the




**5**

alkyl groups R and R′ are in the more stable W-configuration and that it is free to close to either *cis*- or *trans*-dialkylcyclopropane, *sans orbital-symmetry factors*, then it would seem reasonable that those factors which control the relative thermodynamic stability of the ring closure product (*i.e.*, of $\Delta G_{eq}$) will be playing a role in the transition state leading to those products. If, for example, R and R′ are methyl then it is known that the *trans*-isomer is more stable than the *cis* ($\Delta G_{eq} = 1.0$ kcal mol$^{-1}$) by a factor of 5.5 at 30° (13). Thus if the magnitude of the steric effects were the same for the transition states as for the ground states we would have $\Delta\Delta G^{\ddagger} = \Delta G_{eq}$. This is likely to be too large an estimate and the effect will probably be attenuated. One possible indication of the attenuation is that the ring closure from triplet diradicals (14) gives a 1.55:1 ratio of *trans*- to *cis*-1,2-dimethylcyclopropane and thus $\Delta\Delta G^{\ddagger} = 0.26\ \Delta G_{eq}$. If instead of methyl we consider the case of 1,2-diphenylcyclopropane we find that $\Delta G_{eq}$ is 2.34 kcal mol$^{-1}$ at 205° (15, 16). Upon attenuating this value by 0.26 we find that for every mole of substrate going to a diradical 0.65 mol (or the equivalent of $2k_1$ in Scheme 1) will end up as racemic *trans*-1,2-diphenylcyclopropane and 0.35 mol as the *cis*-isomer. This suggests that the analogous $k_2/k_1$ for the diphenylcyclopropane is such that for any value greater than 1.08 the process is diradical and for smaller values than this that we have some electrocyclic character. The value observed at 205° for the ratio of the rate constants for the loss of optical activity to the rate constant for *trans* to *cis* isomerization (the equivalent of $(2k_1 + k_2)/k_2$ in Scheme 1) is 1.42 (16) which gives a value of $k_2/k_1$ of 4.8. The divinylcyclopropane may be expected to demonstrate steric effects intermediate between the methyl and phenyl groups, and thus assuming a value of $\Delta G_{eq}$ of 1.7 kcal mol$^{-1}$ we get an analogous value for the $k_2/k_1$ ratio of 1.20. The value observed in this work for 1,2-divinylcyclopropane at 160° is 2.8, again implying that the isomerization has no electrocyclic component.

It has been observed that *cis*- and *trans*-2,3-diaryloxiranes have nearly the same equilibrium value as the diarylcyclopropanes (3). Using these arguments we would expect a value of $k_2/k_1 = 1.08$ or greater for a diradical process. The observed value of 0.0045 for *trans*-2-phenyl-3-*p*-tolyloxirane indicates that it has less than 1% diradical character for the racemization process, and it is thus an electrocyclic process (3). There seems to be little evidence that the thermal isomerization of cyclopropanes is an electrocyclic process for Willcott and Cargle (17) found that while their results were most readily rationalized in terms of simultaneously changing the configuration at two of the ring carbons they were not compatible with a preferred dis- or conrotation. Similarly Berson and Balquist (18) and Bergman and Carter (19) have found that their results are more readily rationalized in terms of competitive free rotation and ring closure from a diradical having no

[1]As indicated in the Introduction this assumes that there is no path by which **1** may be converted directly to **3**.

preference for the mode in which the rotation occurs. We conclude that there is no evidence for the use of the *O,O*-trimethylene species in the thermal reactions of cyclopropanes.

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