Thermal Rearrangement of Ethyl 2-Methyl-3-propenylcyclopropanecarboxylates

Paul H. Mazzocchi* and Henry J. Tamburin[1]

Contribution from the Department of Chemistry, University of Maryland, College Park, Maryland 20742. *Received August 15, 1974*

Abstract: Thermal rearrangement of each of the four isomeric ethyl 2-methyl-3-(*trans*-propenyl)cyclopropanecarboxylates resulted in cis–trans isomerization to the other isomers and to the formation of a number of rearrangement products. These were identified as ethyl *cis,trans*- and ethyl *trans,trans*-2,5-dimethyl-3-cyclopentene-1-carboxylate, ethyl 2-ethyl-(*E,E*)-2,4-hexadienoate, ethyl 2-vinyl-*cis*-3-hexenoate, and ethyl 3-vinyl-*trans*-4-hexenoate. The formation of the cyclopentenes on thermal rearrangement of the vinylcyclopropanes is discussed, and a mechanism based on the intermediacy of a pair of stereochemically distinct diradicals is proposed.

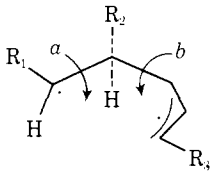
The thermal isomerization of vinylcyclopropanes to cyclopentenes has been the subject of numerous investigations, but the mechanism is still unclear.[2,3] Possible alternatives are a biradical mechanism and either of the symmetry-allowed 1,3 sigmatropic processes.[4] In theory, the question can be solved by thermolysis of a set of maximally labeled vinylcyclopropanes[4] and correlation of starting material and product stereochemistry; however, the problem is complicated by the fact that vinylcyclopropanes undergo cis–trans isomerization at rates that surpass or favorably compete with rearrangement to cyclopentenes[4,5] so that any stereochemical labels are rapidly lost. Current thought favors a diradical mechanism, and recent work on the related *N*-arylidene-2,2-diphenylcyclopropylamines[6] indicates that cis–trans isomerization and rearrangement to azacyclopentenes probably arises from the same intermediate, presumably a diradical. We have been able to show[7] that a set of maximally labeled vinylcyclopropanes do not undergo rearrangement solely *via* either of the allowed 1,3 sigmatropic processes, and that our thermolysis results are best explained by a set of biradicals subject to hindered rotation and closure modes.

Discussion

The mechanism of the vinylcyclopropane–cyclopentene rearrangement is perhaps best discussed in relation to the reasonable mechanistic alternatives available.

One of these is that the reaction proceeds *via* one of the allowed symmetry controlled concerted processes. In this context, it has been demonstrated that in many cases the activation energy differences between concerted and biradical processes are very small.[8,9] In the case of the tricyclo[3.3.0.0^{2,6}]oct-3-ene, Frey and Hopkins[8] found that the activation energy for this nonconcerted process was only 1 kcal above the related concerted process in bicyclo[2.1.1]hexene.[10] Although symmetry-allowed reactions usually occur with significant stereospecificity, it has been demonstrated that extrasymmetric steric factors can force these reactions to take place *via* diradical pathways.[9,11,12]

For the alternative diradical mechanism, expectations from a classical freely rotating diradical in which initial stereochemistry becomes totally randomized must be qualified. In the diradical derived from a substituted vinylcyclopropane **1**, barriers to rotation around bonds *a* and *b* will differ depending on the nature and initial stereochemistry of the substituents and should affect product distributions.



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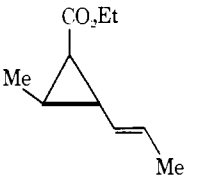
A third alternative involves a mixture of concerted and nonconcerted pathways. This alternative, although intrinsically reasonable, is one which allows for such latitude in possible interpretations that it cannot be critically evaluated with the data at hand.

Thermal Rearrangement of Isomers 2–5. Thermolyses were carried out under essentially two sets of conditions: in sealed tubes for temperatures below 300° and for long reaction times, and in a flow system (short reaction time) at higher temperatures. Preliminary thermolysis of a mixture of **2** (57%) and **3** (43%)[13] at 285° in sealed tubes for 20 hr



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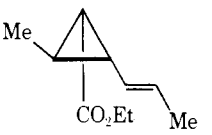

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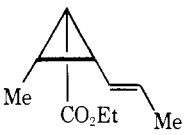

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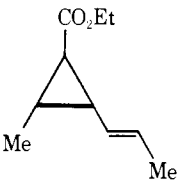

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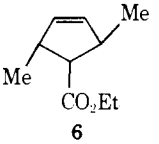
resulted in the formation of four products which were isolated by preparative glpc. The compounds corresponding to the two early retention time peaks were identified as cyclopentenes **6** and **7** (*vide infra*). The material which eluted first from the glpc column showed nmr resonances at τ 4.52 (singlet), a multiplet at τ 7.07, a triplet at τ 8.03 (J = 8.0 Hz), and a doublet at τ 8.87 (J = 7.0 Hz) in addition to expected resonances due to the ethyl group at τ 8.75 and 5.85. The spectrum of the material corresponding to the longer retention time peak showed a singlet at τ 4.48, a multiplet at τ 6.9, an unsymmetrical triplet at τ 7.36 ($J \simeq 9$ Hz), and a pair of doublets (J = 7.0 Hz) at τ 8.94 and 9.12 assigned to the methyl groups.

Consideration of the symmetry properties of the possible isomers **6–8** leads to the unequivocal assignment of the lat-



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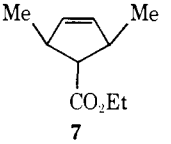

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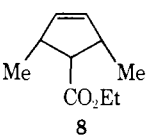

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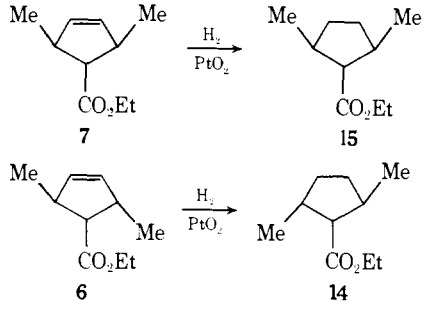
ter material as **6** since only it should show two distinct

methyl resonances. Assignment of the remaining cyclopentene as either **7** or **8** *via* nmr was precluded by the known variations in cis and trans vicinal coupling constants in these systems.[14]

Conclusive proof of the stereochemistry of the cyclopentene pyrolysis products follows from their hydrogenation to the cyclopentanes of known stereochemistry.[15] Accordingly the remaining cyclopentene isomer was identified as **7.**



The longer retention time peaks from the pyrolysis were assigned the structures **9** and **10.** The nmr spectrum of **9** showed a multiplet at τ 4.0–5.2 (5 H), a multiplet at τ 6.7–7.0, and doublets at τ 7.69 (J = 7.0 Hz) and 8.33 (J = 4.5 Hz), whereas its infrared spectrum showed absorption at 1740, 990, 968, and 920 cm^{-1}, consistent with the assigned structure.

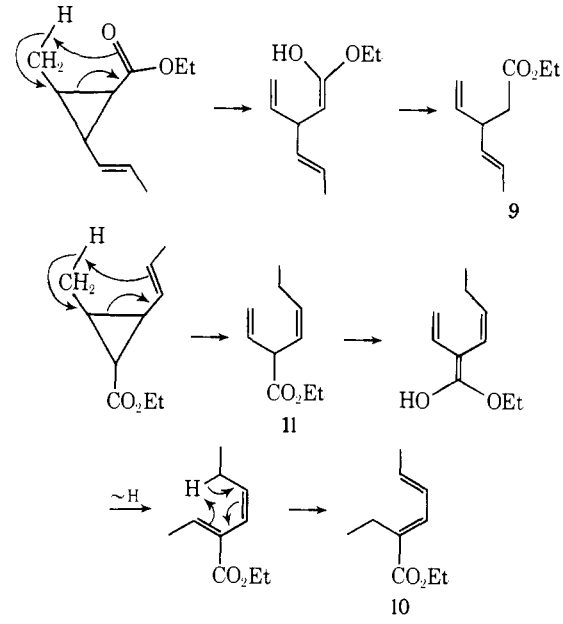
The structure of **10** follows from its hydrogenation to ethyl 2-ethylhexanoate, which establishes the carbon skeleton, and spectral data. The nmr spectrum of **10** showed a quartet at τ 7.62 and a triplet at τ 8.98 corresponding to the C-ethyl group, and a doublet at τ 8.15 (3 H, J = 6.0 Hz) which was assigned to the vinyl methyl group. The vinyl protons appeared as a multiplet at τ 3.40–4.20 and a doublet at τ 2.92 (J = 10.5 Hz) characteristic of a cis β hydrogen in α,β unsaturated esters.[16] Further evidence for the E,E stereochemistry of **10** is afforded by its infrared spectrum which shows a strong 970-cm^{-1} band and its ultraviolet spectrum [λ_{max} (EtOH) 264 nm (ϵ 23,900)]. The related methyl (*E,E*)-2,4-hexadienoate[17] shows its maximum at 258.5 nm, and the addition of an alkyl group predicts a value of 263.5 nm, consistent with the observed value for **10.**

When flow thermolysis conditions (480°) were used, a new product, in addition to the cyclopentenes **6** and **7,** was formed and assigned structure **11** on the basis of its hydrogenation to ethyl 2-ethylhexanoate and spectral data. The infrared spectrum of **11** showed characteristic bands at 990 and 920 cm^{-1}, and the nmr showed a multiplet at τ 3.8–5.2 (5 H), a pentuplet at τ 7.90 (2 H), and a triplet at τ 9.02 (3 H).

The absence of **11** from the long reaction time (285°) thermolysis and its presence under flow conditions suggest that it may be the initial product which undergoes further reaction under the former conditions to **10** *via* the route outlined in Chart I. To test this point, a sample of **11** was heated at 300° in a sealed tube for 1.5 hr. Analysis of the pyrolysate by glpc indicated that *ca.* 70% of the product consisted of **10.**[18]

The important point to be made here is that the hydrogen migration product **11** can only be formed from those cyclopropanes which have cis methyl and propenyl groups[19a-e] and **9** can only be formed from those which have cis methyl and carbethoxy groups.[19f-h] It should also be pointed out here that if formation of cyclopentenes proceeds *via* a biradical, it must be the one which arises from the S-cis conformation of the propenyl group, the same conformation which is necessary to the formation of **11.** Cleavage to a biradical

Chart I



via the S-trans conformation can only lead to cis-trans isomerization since cyclopentene formation is precluded by the fact that it would result in a trans double bond in the cyclopentene ring.

In fact the formation of **11** can be used as a dynamic internal standard during the course of the reaction since it represents the amount of **5** (or **4**) present in the thermally equilibrating mixture of vinylcyclopropanes as the reaction proceeds. The same argument holds true for **9** with respect to **2** (or **4**), and this is the basis on which the analysis of the pyrolysis products from **2–5** is based (vide infra).

Synthesis of the Isomeric Ethyl 2,5-Dimethylcyclopentene- and 2,5-Dimethylcyclopentanecarboxylates. The absence of the cyclopentene **8** under the reaction conditions is unfortunate in that it allows the possibility that **8** is unstable to these conditions and isomerizes to the isomer **7.** To gain some insight on this point, we attempted an independent synthesis of **8** to test its stability to the reaction conditions. The synthesis of the corresponding saturated esters of the 2,5-dimethylcyclopentanecarboxylic acids[15] was also carried out as a model for the cyclopentene synthesis and to serve as authentic samples in the structure identification of **6** and **7** (vide supra). The routes used are outlined in Charts II and III.

Chart II

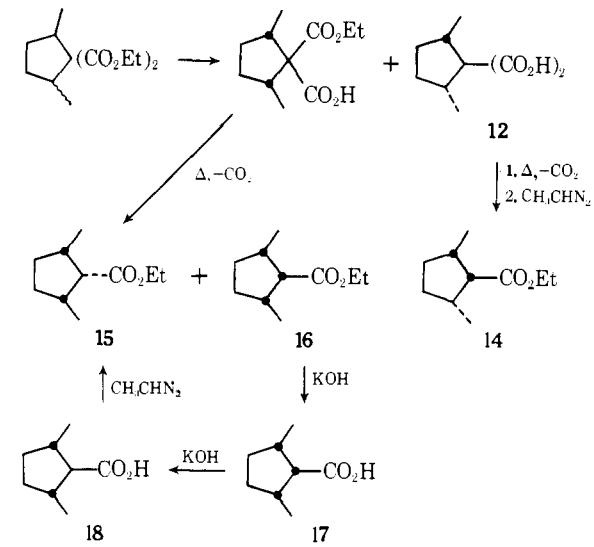
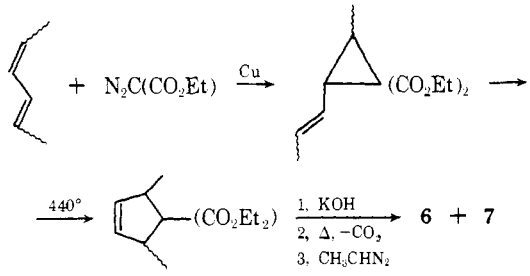


Chart III



The cyclopentanes **14–16** were prepared by the method of Jacobs and Florsheim[15] as outlined (Chart II). Decarboxylation of **12** followed by diazoethane esterification gave the desired ester **14.** Decarboxylation of the half ester **13** afforded a mixture of esters **15** and **16** in a 1.2:1 ratio, respectively. The stereochemical assignment was based on hydrolysis and base-catalyzed epimerization of the major isomer **16** to the more stable **15** as shown.

The cyclopentenes were obtained *via* a route entailing pyrolysis of the diesters obtained from the copper-catalyzed addition of ethyl diazomalonate[20] to equilibrated 2,4-hexadiene[21] and afforded a mixture of dimethylcyclopentene diesters in 55% yield.[22] It is noteworthy that the product may be obtained in essentially pure form by distillation of the pyrolysate and is uncontaminated by dienes. Obviously the addition of a second ester group sufficiently stabilizes the intermediate (diradical?) that the concerted hydrogen migration processes are no longer competitive. This material was subjected to basic hydrolysis, decarboxylation, and the esterification under conditions which afford the three isomeric cyclopentane analogs. The product was worked up *via* preparative glpc, and cyclopentenes **6** and **7** were isolated. On careful analysis of the remaining material by nmr, we were unable to detect any of the desired **8.**

It is possible that the absence of **8** in the cyclopentenes is due to increased steric interaction present in **8** *vis-à-vis* **16.** Whereas the methyl groups in **16** adopt an equatorial position, the more planar cyclopentene ring should increase the interaction of the methyl and carbethoxy groups. Steric interaction with the potential cis carbethoxy group should develop earlier along the reaction coordinate and result in an increase in the activation energy for the formation of **8** as opposed to **7.**

The alternative explanation, that initially formed **8** isomerizes to the more stable **7,** is doubtful in view of the fact that the analogous saturated ester **16** is isolable under similar reaction conditions.

Thermal Rearrangement of the Isomers 2–5. Comparative Runs. Thermal rearrangement of each of the pure isomers **2–5** was carried out on dilute solutions of the vinylcyclopropane in cyclohexane at 480° in a flow system. Products were analyzed by glpc under conditions known to separate all the isomers. The runs at 285° were carried out for 35 min in sealed glass tubes. Under these conditions, isomerization to the other cyclopropane products had proceeded to the extent of *ca.* 10%, and the major component was still unreacted starting material. As pointed out previously, **11** is unstable under these reaction conditions, isomerizing to **10,** whereas at higher temperatures **9** is a very minor product whose relative concentration was not determined.

In one instance in the 480° runs, the reaction was carried out in the presence of an internal standard (undecane). Integration of the glpc trace indicated a material balance of >70% indicating that, although there was some material loss to polymerization, the products being analyzed were real and not minor impurities which had somehow become concentrated during the reaction procedure. The major barrier to the interpretation of the stereochemical results from thermolysis of labeled vinylcyclopropanes is the competing geometrical isomerization of starting material. Indeed, in previously reported attempts at solution of the problem, geometrical isomerization was found to be much faster than rearrangement to cyclopentenes.[3,5] In the system under consideration, geometrical isomerizations proceeding *via* cleavage of the most labile cyclopropyl bond may be characterized as operations requiring rotation of a single substituent (peripheral equilibria, Figure 1) or rotation of a pair of substituents (diagonal equilibria, Figure 1) with respect to the cyclopropyl methyl group, and it is these processes that make it difficult to determine the true precursor of the cyclopentenes. In the absence of the improbable set of circumstances that one might find a system where rearrangement to cyclopentenes is significantly faster than geometrical isomerization, there are at least two other solutions to the problem. In the first case, one might thermolyze each of the vinylcyclopropanes to very low conversion and attempt to determine the rates of isomerization to the terminal products **6–7** and to the isomeric vinylcyclopropanes. This information, although difficult to obtain, might allow analysis of the mechanistic alternatives.

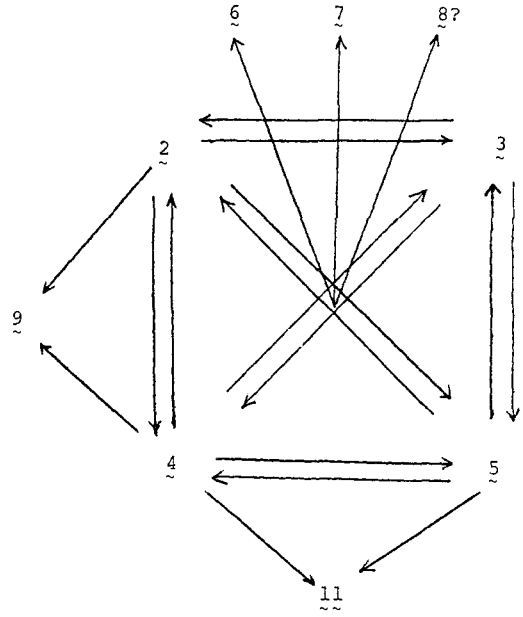


Figure 1. Possible routes for the interconversion of **2–5** and for the formation of products **6, 7, 9,** and **11.**

Our approach was somewhat simpler, if more limited in scope, and can only address the problem in terms of the reaction occurring essentially *via* a single mechanism. We make use of the fact that the retroene products **9** and **11** can only arise from the vinylcyclopropanes with cis carbethoxy and methyl groups (**2** and **4**) and cis propenyl and methyl groups (**4** and **5**), respectively. Since the formation of these materials is essentially irreversible, **9** can be used as a measure of the **2** and **4,** and **11** of the **4** and **5** formed as the reaction proceeds.

The symmetry-controlled rearrangement of isomers **2–5** can occur either antarafacially with retention of stereochemistry at the migrating carbon or suprafacially with inversion at the migrating carbon. The suprafacial-retention process is a symmetry-forbidden one which must be considered in view of the Berson-Salem subjacent orbital approach.[23] Predictions are outlined in Table I.

Examination of the thermolysis results obtained (Table II) allows one immediate conclusion; the reaction does not take place *via* a common intermediate nor can there be a preequilibrium which randomized the stereochemistry of

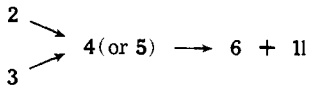
Table I. 1,3 Migration Products

Starting material	Antarafacial inversion	Antarafacial retention	Suprafacial inversion	Suprafacial retention
2	6	6	7	8
3	6	6	8	7
4	7	8	6	6
5	8	7	6	6

the starting vinylcyclopropanes prior to their isomerization to cyclopentenes as each of these cases would afford identical ratios of **6** and **7** irrespective of starting material.

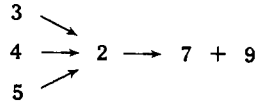
The possibility that the reaction proceeds wholly *via* symmetry-allowed processes in combination with a series of convenient geometrical isomerizations of the starting cyclopropanes may be excluded by examination of the ratios of **9** and **11** to **6** and **7**.

For example, the possible inversion route for the formation of **6** from **2** and **3** could take place *via* preliminary isomerization to **4** or **5**. However, **4** and **5** afford rather large amounts of **11**, and the intermediacy of **4** or **5** as the



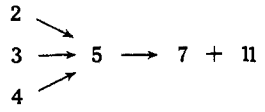
precursor of **6** would require that the **11**/**6** ratio be as large for **2** and **3** as it is for **4** or **5**.

A similar argument may be presented against the formation of **7** in a symmetry-controlled process by prior isomerization to **2**. The results at 285° clearly rule out this process for **3**. Whereas **9** is the major product on thermolysis of **2**



under these conditions, it is a minor product from **3**, *i.e.*, **2** cannot be the only precursor of **7**.

With respect to the possible symmetry-controlled retention route, a prior isomerization may be ruled out by considering the **11**/**7** ratio from pyrolysis of **2** and **3**. Clearly



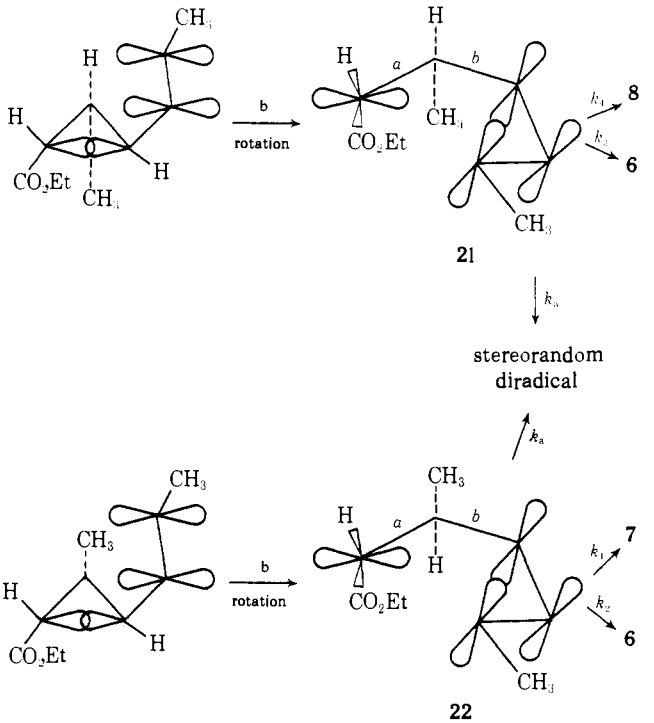
prior isomerization to **5** as the only route to **7** requires that the **11**/**7** ratio for **2** and **3** be the same as for **5**, and this is not the case.

There also appears to be little correlation with predictions based on subjacent orbital considerations.

Although a reaction proceeding totally *via* a single concerted process is ruled out, numerous sets of unique mixtures of concerted and biradical processes could probably be generated to fit these data. We believe that the following explanation based on diradical intermediates subject to hindered rotations is more economic and best explains the observed results.

Examination of Table II indicates that compounds **3** and **5** in which methyl and carbethoxy groups on the cyclopropane are trans afford the greatest proportion of **7** in which these groups are also trans. Similarly **2** and **4**, in which there are cis methyl and carbethoxy groups, afford an increased proportion of **8** which has one methyl cis to the carbethoxy group, *i.e.*, there appears to be a "memory" effect which relates the starting-material and product stereochemistries. These results can be rationalized on the basis of a model involving C-C bond cleavage, rotations around bonds *a* and/or *b* in the diradical (*i.e.*, **21** or **22**) formed, and closure to cyclopentenes with stereochemical discrimination occurring at the latter two steps. This sequence, for **2** and **5**, is outlined in Chart IV.

Chart IV



Initial cleavage of the C-C bond in **2** and subsequent rotation around bond *b* will afford biradical **21**. To the extent that rotations around *a* and *b* are rapid with respect to ring closure ($k_a > k_1 - k_4$), escape to a stereochemically randomized biradical will occur in which case stereochemical discrimination can only take place during the closure step. To the extent that rotations around *a* are slow with respect to closure and *b* rotations, the intermediate will exhibit stereochemical discrimination or "memory."

Preferred rotational modes in 1,3 biradicals have been demonstrated,[24,25] and these effects have recently been quantified for several substituents.[5] Intuitively one might expect that the mass or steric bulk of the rotating group should be an important factor; *i.e.*, *a* rotation should be slower than *b* rotation.

Table II

Starting material	Relative yields 7	6	11	11/7	9	T, °C
2	1.37 ± 0.04	1.00	5.6 ± 0.8	4.1 ± 0.6		480
3	1.63 ± 0.03	1.00	5.3 ± 0.6	3.2 ± 0.4		480
4	1.30 ± 0.08	1.00	8.8 ± 1.0	6.8 ± 0.8		480
5	1.77 ± 0.11	1.00	11.7 ± 1.5	6.6 ± 0.9		480
2	1.46	1.00			11	285
3	1.75	1.00			~0.5	285

For those biradicals in which closure is fast with respect to rotation around *a*, the reaction may be analyzed with respect to intermediates **22** (from **3** and **5**) and **21** (from **2** and **4**). In the closure process, **21** may close to **6** and **8** and **22** to **6** and **7**, but these modes are nonequivalent. For example, in the transition state for closure to **6**, there is a strong 1,2 methyl-carbethoxy eclipsing interaction that is not present in closure to **7**. Similar arguments indicate that **6** should be strongly favored over **8** on closure of **21**; *i.e.*, in the transition state for closure to **8** a 1,2 methyl-carbethoxy and a 1,3 methyl-methyl interaction, not present in the formation of **6**, are developing. Clearly **21** will show a preference for closure to **6**. The "memory" effect then arises from the fact that **2** and **4** will preferentially react *via* **21** favoring the production of **6**, and **3** and **5** will preferentially react *via* **22** favoring **7**.[26] Those species reacting *via* a direct route (*e.g.*, **2** → **21** → **6** or **8**) are superimposed on that portion of the reaction which proceeds *via* the stereorandomized diradical (*a* and *b* rotation) to afford the observed product distribution. Again in this stereorandomized case, interactions during closure of the biradical should cause **7** to predominate over **6** for stability reasons and **6** to predominate over **8** for stability and statistical considerations, *i.e.*, the expected product ratios are always **7** > **6** ≫ **8** as observed.

Experimental Section

Microanalyses were performed by Dr. F. Kasler. The infrared spectra were obtained on a Perkin-Elmer 337 grating infrared spectrophotometer in a 0.1-mm NaCl cell (10% in carbon tetrachloride). The nmr spectra were obtained on a Varian A-60D spectrophotometer in carbon tetrachloride solutions with tetramethylsilane as internal standard. The preparative glpc work was done on a Varian Aerograph Series 90 using a thermal conductivity detector; the analytical glpc work was done on a Varian Aerograph Series 1200 with flame ionization. A list of glpc columns employed follows: column A, 15% IGEPAL (CO-880) on 80–100 Chromosorb W (AW-DMCS), 9 ft × 0.25 in.; B, 11% Carbowax 20M and 4% DEGA on 60–80 Chromosorb W (AW-DMCS), 6 ft × 0.25 in.; C, 15% UCON 50 HB 270X on 80–100 Chromosorb W (AW-DMCS), 15 ft × 0.25 in.; D, 15% UCON 50 HB 270X on 60–80 Chromosorb W (AW-DMCS), 6 ft × 0.125 in.; E, 15% UCON 50 HB 270X on 60–80 Chromosorb W (AW-DMCS), 6 ft × 0.25 in.; F, 15% Carbowax 20M on 60–80 Chromosorb W (AW-DMCS), 9 ft × 0.125 in.; G, 15% silicone D.C. 550 on 60–80 Chromosorb W (AW-DMCS), 6 ft × 0.25 in.; H, 10% SE-30 on 100–120 Chromosorb P (AW-DMCS), 10 ft × 0.125 in.

Thermolysis of Vinylcyclopropanes 2 and 3. A mixture consisting of 43% **3** and 57% **2** (200 μl.) was heated at 290–300° for 20 hr in a stainless steel bomb. Analysis of the pyrolysate on column D (100°) indicated four major peaks present with retention times of 10.5, 12.5, 16.5, and 38.0 min in relative amounts of 3.6:2.3:5.1:1.0, respectively. Samples of the material corresponding to the three short retention time peaks were collected together from column E, (130°) then separated and purified on column A (90°).

The compound corresponding to the 10.5-min peak was identified as ethyl *trans,trans*-2,5-dimethyl-3-cyclopentene-1-carboxylate (**7**) on the following basis: nmr signals appeared at τ 4.52, singlet (2 H, vinyl), 5.85, quartet (2 H, J = 7.0 Hz, $-COOCH_2CH_3$), *ca.* 7.07 (6.80–7.40), overlapping quartets (2 H, J_{bc} = 7.0, J_{ba} = 8.0 Hz, allylic H_b), 8.03, triplet (1 H, J_{ab} = 8.0 Hz, tertiary methine), 8.75, triplet (3 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.87, doublet (6 H, J_{bc} = 7.0 Hz, allylic methyl).

An infrared spectrum showed characteristic bands at 3070 (vinyl C–H stretch), 2980, 2950, 2930, 2900 (saturated C–H stretch), 1740 (carbonyl stretch), 1600 (C=C stretch), and 1175 cm^{-1} (C–O–C stretch).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 71.39; H, 9.59. Found: C, 71.11; H, 9.34.

The stereochemistry of cyclopentene **7** was confirmed further by hydrogenation to cyclopentane isomer **15** (*vide infra*).

The compound corresponding to the 12.5-min peak was obtained pure after a second pass on column A. The material was identified as ethyl *trans,cis*-2,5-dimethyl-3-cyclopentene-1-carboxylate (**6**). Nmr signals appeared at τ 4.48, singlet (2 H, vinyl), 5.87, quartet (2 H, J = 7.0 Hz, $-COOCH_2CH_3$), *ca.* 6.90 (6.60–7.20), multiplet (2 H, allylic) and 7.36, quartet (1 H, J = 9.0 Hz, tertiary methine), 8.73, triplet (3 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.94, doublet (3 H, J = 7.0 Hz, allylic CH_3), 9.12, doublet (3 H, J = 7.0 Hz, allylic CH_3).

An infrared spectrum showed characteristic bands at 3050 (vinyl C–H stretch), 2970, 2930, 2900, 2870 (saturated C–H), 1745 (carbonyl stretch), 1605 (C=C), and 1180 cm^{-1} (C–O–C).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 71.39; H, 9.59. Found: C, 71.15; H, 9.48.

Hydrogenation of this material afforded the *trans*-dimethylcyclopentane **14** (*vide infra*).

The compound corresponding to the 16.5-min peak was identified as ethyl 3-vinyl-*trans*-4-hexenoate (**9**) on the following basis: nmr signals appeared at τ 4.00–5.20, multiplet (5 H, vinyl), 5.93, quartet (2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 6.70–7.00, multiplet (1 H, doubly allylic), 7.69, doublet (2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 8.33, broadened doublet (3 H, J = 4.5 Hz, vinyl methyl), 8.78, triplet (3 H, J = 7.0 Hz, $-COOCH_2CH_3$).

The infrared spectrum showed characteristic absorption at 3080 (terminal vinyl C–H stretch), 3010 (vinyl C–H), 2975, 2935, 2910 (saturated C–H), 1740 (carbonyl), 1635 (C=C stretch), 990, 920 (terminal vinyl C–H bend), and 968 cm^{-1} (trans-substituted olefinic C–H wag).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.63; H, 9.60.

The compound corresponding to the long retention time peak was identified as ethyl 2-ethyl-(*E,E*)-2,4-hexadienoate (**10**) from exact retention times of authentic material prepared as follows. A 250-μl. sample of vinylcyclopropane isomers **4** and **5** was thermolyzed as above at 300° for 4 hr. Analysis of the pyrolysate on column D (100°) showed two major products (retention time 13.0 and 36 min in a relative ratio of 1.5:1.0, respectively).

The shorter retention time peak was the expected 1,5-hydrogen migration product **11** (*vide infra*). The longer retention time peak was collected and purified on column A (110°) and identified as **10** on the basis of the following infrared spectrum: maxima at 3030 (vinyl C–H), 2970, 2940 (saturated C–H), 1705 (carbonyl stretch), 1230 (methyl bend), and 970 cm^{-1} (vinyl C–H bend). The nmr spectrum showed resonances at τ 2.92, doublet (1 H, J = 10.5 Hz, vinyl H_a), 3.40–4.20, complex multiplet (2 H, vinyl H_b and H_c), 5.83, quartet (2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 7.62, quartet (2 H, J = 7.0 Hz, methylene), 8.15, doublet (3 H, J = 6.0 Hz, vinyl methyl), 8.72 triplet (3 H, J = 7.0 Hz, $-COOCH_2CH_3$), and 8.98, triplet (3 H, J = 7.0 Hz, methyl). The ultraviolet spectrum showed λ_{max} (EtOH) 264 nm (ϵ 23,900). Hydrogenation of **10** (0.9 μl) in ethanol over PtO_2 at atmospheric pressure afforded ethyl 2-ethylhexanoate as evidenced by glpc.

Ethyl 2-Vinyl-*cis*-3-hexenoate (11). This compound was conveniently obtained on a large scale by thermolysis. A sample of 4.2 g of ethyl 2-propenyl-3-methyl-1-cyclopropanecarboxylate at 440° was treated *via* the flow thermolysis procedure. The pyrolysate was distilled, and the fraction, bp 77–79° (7 mm), was collected (1.5 g) and analyzed by glpc on column D (105°). Nine peaks were present, and the compound corresponding to the largest peak (≃50% of total products) was collected by preparative glpc on column E (105°) and purified further on column B (95°).

The nmr spectrum of **11** showed absorption at *ca.* τ 4.50 (3.80–5.20), complex multiplet (5 H, vinyl), 5.90, quartet (2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 6.00–6.40, multiplet (1 H, doubly allylic), 7.90, slightly split quintet (2 H, allylic methylene), 8.77, triplet (3 H, J = 7.0 Hz, $-COOCH_2CH_3$), and 9.02, triplet (3 H, J = 7.0 Hz, methyl). The infrared spectrum had characteristic bands at 3080 (terminal vinyl C–H), 3010 (vinyl C–H), 2970, 2930, 2865 (saturated C–H), 1740 (carbonyl stretch), 1630 (C=C), 1165 (C–O–C stretch), and 990 and 920 cm^{-1} (terminal vinyl C–H bend).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.52; H, 9.56.

Hydrogenation of a sample of **11** (8 μl., PtO_2–EtOH) afforded material identical (ir, glpc) with ethyl 2-ethylhexanoate.

A sample of **11** (2 μl.) in a glass ampoule was heated at 300° for 75 min. Glpc analysis showed the major product (~70%) to be **10**.

Flow Thermolysis of Cyclopropanes 2–5. The thermolysis was

accomplished in an electric pyrolysis oven containing a Pyrex tube (6 in. × 0.25 in.) packed with ⅛ in. Pyrex helices. The temperature was controlled by a Variac and read from a calibrated thermocouple. The tube and helices were treated with refluxing nitric acid, then washed sequentially with water, ammonium hydroxide, water, and acetone prior to each run.

Sample introduction was accomplished by placing a serum cap at the top of the pyrolysis tube and slowly (2 μl./10 sec) injecting the cyclohexane solution onto the hot helices. The vapors were swept through the oven by the continuous stream of dry nitrogen (46 ml/min) into a pear-shaped flask equipped with a Dry-Ice condenser. Immediately after each run, the pyrolysis tube was flushed with 100 μl. of cyclohexane, and the pyrolysate was then analyzed by glpc on column H (90°). Product ratios were obtained by peak weighing and triangulation. The results of 5–7 runs for each of the isomers **2–5** are presented in Table II.

Thermolyses of Isomers 2 and 3 to Low Conversions. Samples of isomer **2** and **3** (2 μl.) were sealed in separate capillary tubes which were secured to the bottom of a thermometer by wire. A Woods Metal Bath was preheated to 285°, and carefully the thermometer and the tubes were lowered into the bath. After 35 min, the contents were analyzed by glpc on column F (90°). In both cases, the major component in the reaction mixture was unreacted starting material, and the other vinylcyclopropanes were present in amounts estimated to be *ca.* 10% (see Table II).

Hydrogenation of Cyclopentenes 6 and 7. The products (**6, 7,** and **11**) from a sealed tube thermolysis of 100 μl. of **2** and **3** (260–270°, 6 hr) were collected together (column E, 130°). Compound **7** was separated by one pass on column E (100°).

Hydrogenation of this material (8 μl.) at atmospheric pressure (PtO_2–EtOH) afforded one major product (column E, 100° retention time 26 min) which was collected and purified (two passes) on column A (135°). The infrared spectrum and glpc retention time (by coinjection) were identical with those of authentic **14.** The remaining mixture of pyrolysis products which now consisted of **7** (14%), isomer **6** (70%) and the diene **11** (16%) was hydrogenated, and the products were analyzed on column F (100°) and identified by glpc retention times as ethyl 2-ethylhexanoate (18%, 22.5 min), **14** (13%, 26 min), and **15** (69%, 31 min). This latter material was collected on column A (135°) and its infrared spectrum shown to be identical with that of authentic **15.**

Ethyl *cis,trans*-2,5-Dimethylcyclopentane-1-carboxylate (14). Decarboxylation and esterification of **12** according to the procedure of Jacobs and Florsheim[15] afforded **14** which was purified by preparative glpc on column G (125°). The nmr spectrum exhibited absorption at τ 5.91, quartet (2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 7.50–8.40, complex multiplet (7 H, cyclopentyl methylene, cyclopentyl methyl methine, and cyclopentyl carbethoxy methine), 8.76, triplet (3 H, J = 7.0 Hz, $-COOCH_2CH_3$), and 9.07, overlapping doublets (6 H, J = 6.0 Hz, cyclopentyl methyl). The infrared spectrum showed bands at 2960, 2915, and 2875 (C–H stretch), 1730 (carbonyl stretch), 1460, 1375 (methyl C–H bend), and 1160 and 1190 (C–O–C stretch).

Ethyl *cis,cis*-2,5-Dimethylcyclopentane-1-carboxylate (16) and Ethyl *trans,trans*-2,5-Dimethylcyclopentane-1-carboxylate (15). Decarboxylation of the half ester **13**[15] afforded a mixture of **15** and **16** in a 1.2:1 ratio by glpc. Preparative glpc on column C (130°) gave pure material after two passes. Compound **16** had nmr absorptions at τ 5.89, quartet (2 H, J = 7.0 Hz, $-COOCH_2CH_3$), *ca.* 8.20 (7.80–8.80), complex multiplet (7 H, methylene protons, cyclopentyl methyl methine, and cyclopentyl carbethoxy methine), 8.75, triplet (3 H, J = 7.0 Hz, $-COOCH_2CH_3$), and 8.97, doublet (6 H, J = 6.0 Hz, cyclopentyl methyl). The infrared spectrum has characteristic bands at 2955, 2930, 2905, 2875 (C–H stretch), 1730 (carbonyl stretch), 1375, 1450 (methyl C–H bend), and 1160 cm^{-1} (C–O–C stretch).

The major isomer **15** exhibited nmr absorption at τ 5.91, quartet (2 H, J = 7.0 Hz, $-COOCH_2CH_3$), 7.42, multiplet (1 H, cyclopentyl carboethoxy methine), *ca.* 8.10 (7.60–8.50), unresolved multiplet (6 H, cyclopentyl methylene and cyclopentyl methyl methine), 8.75, triplet (3 H, J = 7.0 Hz, $-COOCH_2CH_3$), and 9.02, doublet (6 H, J = 6.0 Hz, cyclopentyl methyl). The infrared spectrum had characteristic bands at 2960, 2940, 2910, and 2860 (C–H stretch), 1730 (carbonyl stretch), 1390, 1460 (methyl C–H bend), and 1150 and 1190 cm^{-1} (C–O–C stretch).

Saponification and epimerization of the original diester mixture with MeOH–KOH, followed by diazoethane esterification, gave essentially pure material identical (glpc, nmr) with the major isomer **15** which establishes its structure. No **16** was detected (<1%) under these conditions.

Diethyl 2,5-Dimethyl-3-cyclopentene-1,1-dicarboxylate (20). Pyrolysis of 22 g of diethyl 2-propenyl-3-methylvinylcyclopropane-1,1-dicarboxylate, prepared from the copper-catalyzed insertion of ethyl diazomalonate to an equilibrated mixture of 2,4-hexadienes, was carried out using a 22 in. helices (3/32 in.) packed tube in a standard Hoskins combustion furnace at 400° in a nitrogen atmosphere.

The pyrolysate was distilled and the fraction by 75–85° (0.5 mm) (12.0 g, 55%), collected as essentially pure **20.**

Hydrolysis and Decarboxylation of 20. A sample of 5.0 g (0.02 mol) of **20** was refluxed for 43 hr with 3.4 g (0.06 mol) of potassium hydroxide in 40 ml of methanol; 15 ml of water was added to the reaction mixture and alcohol removed by vacuum distillation. The solution was brought to a volume of 50 ml by the addition of water, and 6 N HCl was added dropwise until the solution was acid to Congo Red test paper. The solution was extracted with ether and dried ($MgSO_4$) and solvent removed. The residue (4.0 g) which showed acid and vinyl protons in the nmr spectrum was decarboxylated by heating in an acid-washed 100-ml round-bottomed flask at 200–210° for 35 min. Ether was added and the mixture esterified with diazoethane. Distillation of the resulting esterified solution gave 0.6 g of yellow oil, bp 44–50° (0.3 mm). The fraction was analyzed by preparative glpc on column A (90°) and showed two major and four minor products present. The two major products were collected and identified as cyclopentene isomers **6** and **7,** respectively. The minor peaks were also collected, but none showed the characteristic nmr patterns for a 1-carboethoxy-3-cyclopentene.

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Structures of 1,1-Dichloro-2,2-diphenylcyclopropane and 1,1-Dibromo-2,2-diphenylcyclopropane. A Study of Substitution Effects on Cyclopropane Geometries

Joseph W. Lauher and James A. Ibers*

Contribution from the Department of Chemistry and the Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received August 16, 1974*

Abstract: The structures of 1,1-dichloro-2,2-diphenylcyclopropane and 1,1-dibromo-2,2-diphenylcyclopropane have been determined from three-dimensional X-ray data collected by counter techniques. The compounds are isomorphous, crystallizing in the monoclinic space group C_{2h}^5-$P2_1/c$ with four molecules per cell. Cell constants for the chloro derivative are a = 6.170 (2), b = 13.673 (4), c = 15.513 (4) Å; and β = 92.24 (2)°; cell constants for the bromo compound are a = 6.246 (2), b = 13.822 (4), c = 15.640 (4) Å; and β = 93.88 (2)°. The structures have been refined by full-matrix least-squares procedures to conventional R indices of 0.034 (on F) and 0.046 (on F^2) for the chloro compound and 0.035 (on F) and 0.067 (on F^2) for the bromo derivative. Both structures have unsymmetrical cyclopropane rings with C–C bond lengths of 1.490 (3), 1.520 (3), and 1.529 (3) Å in the chloro compound and 1.477 (6) and 1.508 (6), and 1.509 (6) Å in the bromo compound. The longer bonds in the chloro compound may result from withdrawal of electrons from the cyclopropane ring as a whole. In each structure the shortest C–C bond is that across the ring from the point of phenyl substitution. For other cyclopropanes, this shortening has been observed previously across from substituents which can interact through π orbitals and has been explained by simple molecular orbital arguments. Such simple arguments do not explain the shortenings observed for the compounds studied here since the orientations of the phenyl rings do not allow overlap of the appropriate orbitals.

The unique ability of a cyclopropane ring to conjugate with neighboring π orbitals has long been recognized. Spectroscopic and chemical studies of various substituted cyclopropanes have shown that the cyclopropyl group is similar to a double bond in many respects.[1-4] It has been demonstrated that the cyclopropyl group is extremely effective at stabilizing carbonium ions.[1,2]

The molecular structures of numerous substituted cyclopropanes have been reported.[5-14] They show that substitution may cause major changes in the geometry of the cyclopropane ring. In order to assess more fully these effects, we have determined the crystal and molecular structures of 1,1-dichloro-2,2-diphenylcyclopropane and 1,1-dibromo-2,2-diphenylcyclopropane. Our findings are reported here along with comparisons with previously reported structural results.

Experimental Section

The compounds of 1,1-dichloro-2,2-diphenylcyclopropane and 1,1-dibromo-2,2-diphenylcyclopropane were prepared by standard literature methods.[15] Crystals suitable for X-ray work could be obtained from diethyl ether recrystallizations. Preliminary film work indicated that the compounds are isomorphous and crystallize in space group C_{2h}^5-$P2_1/c$.

Lattice parameters were obtained from a least-squares analysis of the setting angles of 16 reflections in the 2θ range 25–30° which had been centered on a FACS-I diffractometer using a takeoff angle of 1.1° and Mo Kα_1 radiation (λ 0.709030 Å) monochromatized from the (002) face of a highly mosaic graphite crystal.[16] The crystal data obtained for each compound are listed in Table I.

The intensity data were collected on the FACS-I diffractometer in shells of 2θ by the θ–2θ scan method using monochromatized Mo Kα radiation. Data collection methods have been detailed previously.[17] The details of the data collections are listed in Table I. During each data collection 6 standard reflections were monitored every 100 reflections and these showed only statistical variations.

The data were processed in the usual manner using a value of 0.04 for p.[16] The chloro compound yielded 2453 unique data which were used in F^2 refinements and 1525 reflections with $F_o^2 > 3\sigma(F_o^2)$, which were used in refinements based on F. The bromo derivative yielded 2396 unique data of which 1490 had $F_o^2 > 3\sigma(F_o^2)$.

The bromo structure was solved by symbolic addition using 299 rescaled values of $E < 1.60$.[18] The chloro derivative was refined first based on the solution found for the bromo compound. Once the refinement of the chloro structure was complete, refinement of the bromo derivative was begun using the final parameters of the chloro structure. Full-matrix least-squares techniques were employed,[17] and the details are listed in Table I. In both cases, the initial cycles of refinement were based on F, using only those reflections having $F_o^2 > 3\sigma(F_o^2)$. Because of the relatively large number of observations not satisfying this condition, final refinements were carried out on F_o^2, using all unique data, including those with $F_o^2 \leq 0$.

Tables II and III list the values of $100|F_d|$ and $100|F_d|$ (in electrons) for the chloro and bromo compounds, respectively.[19] These values are derived from the final cycle of F^2 refinement in each case. Those values of $|F_d|$ less than zero in the tables denote F_o^2 values observed to be less than zero. Tables IV and V list the values of the atomic parameters for the two structures. Table VI presents the root-mean-square amplitudes of vibration for each structure.

Results

The Crystal Structures. The two similar cyclopropane derivatives crystallize with nearly identical structures. Figure 1 presents a stereoview of the unit cell of the chloro derivative. The unit cell of the bromo compound is essentially the same. The packing is dominated by the phenyl rings. The closest intermolecular distances are in each case H–H contacts of about 2.35 Å.

The Molecular Structures. The molecular structures of the two cyclopropanes are similar. A view of the chloro de-