the carbon acid and the solvent are large, protonation rates should be relatively insensitive to solvent acidity.

We have also tried experiments substituting tetramethylammonium as a cation in *tert*-butyl alcohol. This had the effect of increasing the exchange rate by a factor of about 100 but the rate of loss of substrate was not correspondingly increased. The value of k_e/k_h was less than 0.1.

Addition of the remarkable compound "dicyclohexyl-18-crown-6"[6] (0.048 N) to the potassium *tert*-butoxide (0.43 N) catalyzed reaction in *tert*-butyl alcohol-*O-d* increased the exchange rate by a factor of 60. A value of $k_e/k_h = 2$ was observed. A mild decrease in k_e/k_h was also found when cesium was substituted for potassium.

From these results we conclude that protonation is relatively slow when a counterion must be displaced from the reaction site. The alternative explanation in which electron transfer is accelerated by the presence of the counterion seems less logical because, even if both reactions had $\Delta H^{\ddagger} = 0$, protonation should be favored by virtue of concentration. Something must slow protonation to make electron transfer competitive. Electron transfer is apparently slowed by the counterion to a lesser extent than protonation when the counterion is potassium or cesium. This suggests that either the electron is transferred from some remote site in the anion or that electron transfer occurs through the metal ion.

Recent results with substituted fluorenyl systems in methanol[7] have shown that electron transfer from free carbanions can occur, but becomes more efficient when ion pairing is promoted by high cation concentrations. In the case of free triphenylmethide ion, electron transfer to nitrobenzene is apparently very much slower than protonation. When the cation is merely solvated but remains ion paired or when the cation size is increased, protonation is mildly accelerated relative to electron transfer.

The potential of electron-transfer experiments for probing carbanion chemistry is becoming increasingly apparent. Preliminary results in several new systems suggest wide applicability.

Acknowledgment. We wish to thank the National Science Foundation for a grant (GP-17465) supporting this work.

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(6) (a) C. J. Pederson, *J. Amer. Chem. Soc.*, **89**, 2495 (1967); (b) C. J. Pederson, *ibid.*, **89**, 7017 (1967). We thank Dr. K. Frensdorff and Dr. R. T. Uyeda of du Pont de Nemours and Co. for a sample of this material.

(7) R. D. Guthrie and A. T. Young, unpublished results.

Robert D. Guthrie
Department of Chemistry, University of Kentucky
Lexington, Kentucky 40506

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On the Mechanism of the Vinylcyclopropane–Cyclopentene Rearrangement. Evidence Against a Concerted Process

Sir:

The mechanism of the thermal isomerization of vinylcyclopropanes to cyclopentenes has been a perplexing problem to organic chemists. Current thought favors the intermediacy of a diradical rather than a concerted process[1] and this view is supported by activation-energy data and by experiments which indicate that the degenerate rearrangement of vinylcyclopropane proceeds *via* such an intermediate.[2] Consideration of the transition states necessary for possible concerted processes suggests that they may be energetically unfavorable but this is not necessarily a convincing argument.[3] In fact there are no definitive data available which demonstrate the absence of a concerted route for this rearrangement.

Preparation of the isomeric ethyl 2-methyl-3-(*trans*-propenyl)cyclopropane carboxylates (**1–4**) was achieved in yields approaching 59% by the copper-catalyzed insertion of ethyl diazoacetate[4] into *trans,trans*- or *cis,trans*-2,4-hexadiene. Separation was accomplished by preparative glpc on a 15 ft × $^1/_4$ in. column packed with 15% UCON HB270X on 80–100 mesh Chromosorb W. The structures of isomers **1–4** follow from their method of synthesis and analysis of their infrared and nmr spectra,[5] especially the specific deshielding of H_a by the *cis*-carbethoxy groups in **1** and **3**.[6]

The thermal reactions of **1–4** are characterized by their ready isomerization to each other and to products **5–8**.[7] Dienes **5** and **6** are recognizable as 1,5-homocyclic hydrogen migration products and are prevalent products on pyrolysis of *cis*-2-methylvinylcyclopropane[8,9] and alkyl *cis*-2-methylcyclopropane carboxylates,[10] respectively. That the cis relationship of propenyl and methyl groups for isomerization to **5** and of carbethoxy and methyl groups for isomerization to **6** is crucial for these rearrangements has been amply demonstrated[9,10] and it is on this fact that our analysis is based. The ratios of the dienic products **5** and **6** to cyclopentenes **7** and **8** on pyrolysis of each of the isomers **1–4** is unique and their analysis allows a definitive statement on the mechanism of the formation of **7** and **8**.[11]

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(1) S. Sarel, J. Yovell, and M. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, **7**, 577 (1968).

(2) M. R. Wilcott and V. H. Cargle, *J. Amer. Chem. Soc.*, **91**, 4311 (1969); **89**, 723 (1967).

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

(4) H. Musso and U. Biethan, *Chem. Ber.*, **97**, 2282 (1964).

(5) The structures of all new compounds were consistent with their spectral and analytical data. Full experimental details will be published elsewhere.

(6) Additional evidence for the stereochemistry of **2** follows from the thermolysis results (285°) where **2** readily affords the 1,5-homocyclic hydrogen migration product **6** indicating that the methyl and carbethoxy groups are cis to each other.

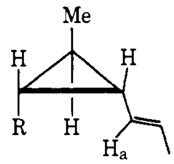
(7) The fact that all of these processes are competitive suggests that they have similar activation energies, *i.e.*, in the range of 30–35 kcal. This is consistent with the expected increased stabilization of an intermediate diradical by carbethoxyl substitution. Also of interest is the fact that the corresponding 1,1 diester affords *only* cyclopentenes on pyrolysis.

(8) R. J. Ellis and H. M. Frey, *Proc. Chem. Soc.*, 221 (1964).

(9) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969); M. J. Jorgenson and A. F. Thacher, *Tetrahedron Lett.*, 4651 (1969).

(10) D. E. McGreer, N. W. K. Chiu, and R. McDaniel, *Proc. Chem. Soc.*, 415 (1964); R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967); W. Ando, *Tetrahedron Lett.*, 929 (1969).

(11) The structures of **7** and **8** were demonstrated by hydrogenation (Pt/EtOH) to the cyclopentanes of known stereochemistry: T. L. Jacobs and W. L. Florsheim, *J. Amer. Chem. Soc.*, **72**, 256 (1950). We have been unable to detect the all-cis isomer **9** in the reaction mixture although it may be present as a minor product. The presence of **9** as, at most, a minor product and the preponderance of **7** is consistent with a transition state for cyclopentene formation which reflects product stability.



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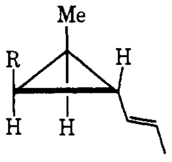

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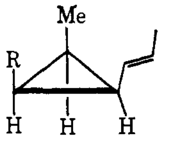

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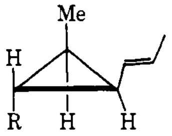

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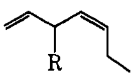

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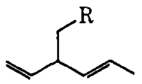
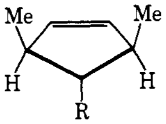
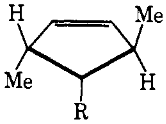


6

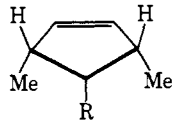
R = CO_2Et



7



8



9

Pyrolysis of 2–5% cyclohexane solutions of isomers **1**–**4** in a flow system at 480 ± 5° followed by glpc analysis[12] gave the results indicated in Table I.

Table I

Starting material	Relative yields 7	8	5	5/7	6	T, °C
1	1.63 ± 0.03	1.00	5.3 ± 0.6	3.2 ± 0.4		480
2	1.37 ± 0.04	1.00	5.6 ± 0.8	4.1 ± 0.6		480
3	1.30 ± 0.08	1.00	8.8 ± 1.0	6.8 ± 0.8		480
4	1.77 ± 0.11	1.00	11.7 ± 1.5	6.6 ± 0.9		480
1	1.75	1.00			~0.5	285
2	1.46	1.00			11	285

The two symmetry-allowed processes for the formation of cyclopentenes from vinylcyclopropanes are 1,3-sigmatropic migrations which may occur either antarafacially with retention of stereochemistry at the migrating carbon, or suprafacially with inversion of stereochemistry at the migrating carbon.[3,13] The predicted products from **1**–**4** *via* these concerted routes are outlined in Table II and the experimental results must be considered in relation to these predictions. We conceive of three possibilities: (1) the reaction is concerted and takes place *via* either of the allowed concerted processes; (2) the reaction is nonconcerted and takes place *via* a diradical intermediate; (3) a mixture of these mechanistic pathways is in effect. Consideration of the information in Tables I and II allows us to rule out the first of these possibilities[14] but we are unable to comment on the last.

Table II

Starting material	Predicted products 1,3 antarafacial (retention)	1,3 suprafacial (inversion)
1	8	9
2	8	7
3	9	8
4	7	8

Table II indicates that although **7** is a symmetry-allowed product of **2** by the inversion mechanism, it is not the predicted product of **1**. The possibility that **7** may arise wholly *via* a **1** → **2** → **7** process may be ruled out on the basis of the results (Table I) at 285°. Thermolysis of neat **1** and **2** at 285° for 30 min gave **7** and **8**, with **7** as the major cyclopentene product, in addition to the diene **6**.[15] If the assumption that **6** may only arise from **2** is valid, then the **1** → **2** → **7** sequence cannot be in effect to any large extent as it would require that the **7**:**6** ratio be identical for **1** and **2**.

A possible route to **8** from **1** and **2** *via* the "inversion" mechanism might involve preliminary isomerization to **3** (or **4**) followed by rearrangement to **8** (*e.g.*, **1** → **3** → **8**); however, this route also predicts that the **5**:**8** ratio be at least as large for **1** and **2** as it is for **3** (*i.e.*, **3** gives the lowest **5**:**8** ratio of the **3**–**4** pair).

Similarly it can be shown that the cyclopentenes cannot result solely from a 1,3-antarafacial migration. The predicted product from **1** (and **2**) *via* this process is **8**. The **7** formed on pyrolysis of **1** could arise *via* preliminary isomerization to **4** which subsequently rearranges to **7** (*i.e.*, **1** → **4** → **7**) but this requires that the **5**:**7** ratios for **1** and **4** be identical. Alternative processes such as

$$\mathbf{5} \xleftarrow{\text{slow}} \mathbf{3} \overset{\text{fast}}{\rightleftharpoons} \mathbf{4} \xrightarrow{\text{slow}} \mathbf{7}$$

would result in identical **5**:**7** ratios for isomers **1**–**4**. Clearly neither of the allowed 1,3-sigmatropic processes can wholly account for the formation of cyclopentenes **7** and **8** although a combination of concerted and nonconcerted (diradical) processes cannot be ruled out.

In addition our data exclude the intermediacy of a single randomized diradical for this reaction since it would result in the **7**:**8** ratios being identical for isomers **1**–**4**. An explanation for this variation in the **7**:**8** ratios may lie in the fact that there are preferred opening and rotational modes[16] for the newly formed diradical which might prejudice the subsequent closure process if the lifetime of the intermediate were sufficiently short.[17] Due to the complexity of the system we have as yet been unable to completely analyze our results in these terms.

Acknowledgments. We acknowledge the partial support of this work by a grant from the Frederick Gardner Cottrell Fund of the Research Corporation.

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[12] Under the conditions employed both conversion to products and total material recovered was >70% as estimated by glpc.

[13] J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **92**, 1096 (1970); J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968).

[14] W. R. Roth also has results which bear on this problem: W. R. Roth, University of Maryland Seminar, Nov 1969.

[15] These reactions were carried out in sealed glass tubes and, under these conditions, **5** was unstable isomerizing further to ethyl 2-ethyl-2,4-hexadienoate.

[16] R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969); J. A. Berson and J. M. Balquist, *ibid.*, **90**, 7343 (1968).

[17] A referee has pointed out an apparent correlation in that compounds 1 and 4, in which the methyl and carbethoxy groups are trans, give the greatest proportion of 7 in which these groups are also trans. One possible rationalization for this is that it results from preferred rotation of the propenyl group in the (presumed) diradical intermediate.

* Address correspondence to this author.

Paul H. Mazzocchi,* Henry J. Tamburin
Department of Chemistry, The University of Maryland
College Park, Maryland 20742

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