Tetrahedron Letters No.53, pp. 4651-4654, 1969. Pergamon Press. Printed in Great Britain

# STERIC CONSTRAINTS IN THE THERMAL 1,5-HYDROGEN SHIFT OF 1-METHYL-2-VINYLCYCLOPROPANE DERIVATIVES. A POSSIBLE MECHANISTIC DUALITY.

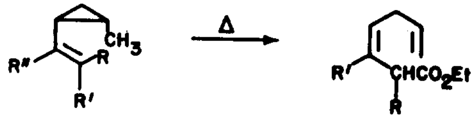
Margaret J. Jorgenson and Anne F. Thacher
Department of Chemistry, University of California
Berkeley, California 94720

(Received in USA 8th August 1969; received in UK for publication 11th October 1969)

The thermal "ene reaction", which takes place with a sigmatropic 1,5-hydrogen shift and concomitant cyclopropane bond cleavage, has been well documented for vinylcyclopropanes constrained into a larger ring (1-4). Roth (5) has drawn attention to the relationship which exists between ring size and reaction ease; the data implicate a stringent spatial requirement for the transition state (6). Grimme (2) has discussed the formation of 1,4-cyclooctadiene from bicyclo[5.1.0]oct-2-ene in similar conformational terms.

The only flexible vinylcyclopropane studied to date is 1-methyl-2-vinylcyclopropane (1) (5,6). The low energy of activation for the cis-isomer constitutes compelling support for the concertedness of the reaction. We have investigated the thermal behavior of six further derivatives (esters 2-4, three isomeric pairs) of 1. The results provide insight into the steric demands of the transition state in flexible systems.

Half-lives for the reaction of esters 2-4 (7) to give dienes 5-7 are recorded in Table I. It is evident that the facility with which the "ene" reaction takes place is related to the substitution pattern about the double bond, particularly that of the terminal olefinic carbon. The large diminution in rate for 4a, by a factor of almost 100 when compared to the related ester 2a, caused by the presence of a cis α-methyl substituent, prompted serious



**1**, R=R'=R''=H
**2a**, R=R''=H; R'=$CO_2Et$
**2b**, R=$CO_2Et$; R'=R''=H
**3a**, R=H; R'=$CO_2Et$; R''=$CH_3$
**3b**, R=$CO_2Et$; R'=H; R''=$CH_3$
**4a**, R=$CH_3$; R'=$CO_2Et$; R''=H
**4b**, R=$CO_2Et$; R'=$CH_3$; R''=H

**5**, R=R'=H
**6**, R=H; R'=$CH_3$
**7**, R=$CH_3$; R'=H

Table I

Reactivity of Cis 1-Methyl-2-vinylcyclopropanes at 200°C[a]

| Compound | Product[b] | Half-life, min.[c] |
|---|---|---|
| 1 | cis 1,4-hexadiene | 29[d] |
| 2a | 5 | 15 |
| 2b | 5 | 35 |
| 3a | 6 | 10 |
| 3b | 6 | 10 |
| 4a | 7 | 1380 |
| 4b | 7 | 120 |

---

[a] Temperature control of ± 1°; 1 µl sample in sealed tube of 3 ml capacity.

[b] Transformations were shown to be quantitative by use of internal standard. Products were characterized spectrally and analytically.

[c] Mixtures of isomers were studied for esters 2 and 3; differences in half-lives between pairs of isomers are real and quite precise. Absolute errors in half-life values could amount to 20-30%, particularly for fast reactions.

[d] Calculated from rate data in references 5 and 6.

consideration of a mechanistic discontinuity. The following data shed light on this possibility. At 305° ester 4a (containing 5% 4c) ring opened at a rate which rapidly decreased with time, the ultimate rate being that with which isomer 4c (8), which possesses a trans disposition of the ring substituents, reacted. Unreacted ester, after 31%, 55%, 67% and 80% conversion to diene proved to consist of a mixture of 4a and 4c in a ratio of 2.6, 1.0, 0.27 and 0.18, respectively. It is evident that an equilibrium ratio of 4a:4c of approximately 15:85 is being approached. This composition is similar to that of the unreacted ester, isolated after one half-life, when pure 4c was reacted at this temperature. Initial rates of formation of 7 from 4a correspond to a half-life of approximately 3 minutes; the trans isomers of 2a (2c), 3a (3c), 3b (3d) and 4a (4c) reacted to furnish 5, 6, 6 and 7, respectively, with corresponding half-lives of 20, 60, 60 and 18 minutes.

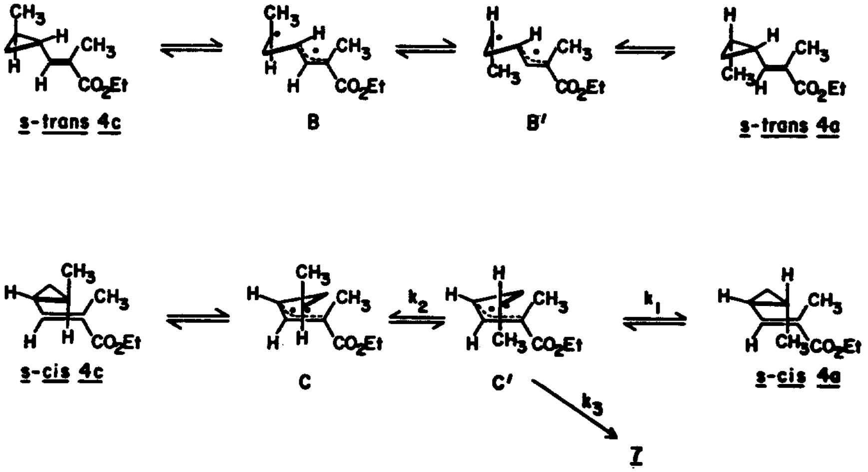
At 200° transformation of 4a (containing 5% 4c) to 7 proceeded with a half-life of 23 hours and was a first order rate process over most of the reaction. Unreacted ester, after 34% and 60% conversion to diene was found to be a mixture of 4a:4c in a ratio of 6.3 and 2.0, respectively. Whereas the character of the reaction of 4a was changed profoundly when carried out in the presence of air at atmospheric pressure at 300°, as were the reactions of trans isomers 2c, 3c, 3d and 4c, the reaction of 4a at 200° was not affected by the presence of air over the first 2-3 half-lives.

From initial rate data it is evident that 4a is transformed into 4c at

300° at approximately half the rate with which 4a yields 7. Geometrical isomerization is less competitive at 200°, proceeding at approximately 1/8 the rate of ring opening to 7. Different entropy requirements for the two reactions could account for the different rate ratios at the two temperatures. Compounded with a rate diminution by a factor of twenty for the transformation of 4c to 7, it is not surprising that at 200°, in contrast to the reaction at 300°, diene formation proceeds from 4a to an overwhelming extent *via* a concerted pathway; isomer 4c should react *via* a diradical intermediate to furnish 7 at a significant rate only at the late stages of the reaction, after its concentration has built up.

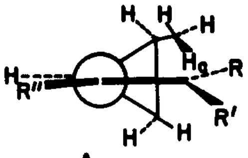
The data suggest that there exists no mechanistic discontinuity between ester 4a and the other esters in the *cis* series (Table I) at 200°. The large rate retardation is probably the result of steric constraints present during the reaction. In geometry A, which can be viewed as an approximation of the transition state, since it permits favorable overlap of all bond orbitals partaking of this transformation, it can be seen that non-bonding interactions between the methyl group, which serves as the terminus of the migrating hydrogen ($H_a$), and the α-$CH_3$ group ($R=CH_3$ in 4a) are severe.

The most economical interpretation of the data at 300° is that transformation of 4a to 7 is still concerted. In this view, the highly competitive interconversion of 4a to 4c proceeds *via* an independent diradical pathway, possibly *via* the *s-trans* conformer of 4a (top of Scheme 1). [Diradicals B and B' cannot furnish 7 directly, since a considerable energy barrier separates B from C and B' from C' (9)]. However, the possibility that there is a change in mechanism and that 4a ring opens to 7 in a diradical mechanism (bottom of Scheme 1) cannot be dismissed on the basis of these data. The observed facile



Scheme 1

geometrical isomerization attests to the ready formation of diradicals from 4a. Diradical C' formed from s-cis 4a may reclose ($k_1$), rotate ($k_2$) (10) or undergo a 1,5-hydrogen shift ($k_3$). In the last process ester 4a would evade the severe steric constraints, which characterize the concerted transformation to 7. (11)



A

Finally, it should be noted that the presence of a carboethoxy group in conjugation with the vinylcyclopropane moiety does not electronically alter the energetics of the ring opening to any significant extent of both the concerted reaction in the cis series as well as that of the diradical reaction in the trans series, compared to the parent system 1 (5).

Acknowledgements: We wish to thank Mr. Jerry Han of this department for his kind and expert assistance with our vapor phase chromatographic separation problems. This research was supported in part by grants from the Petroleum Research Fund of the American Chemical Society (Grant No. 2445-A1,3) and from the National Science Foundation (GP-9443).

## References

1. W. v. E. Doering and W. R. Roth, Angew. Chem. 75, 27 (1963).
2. W. Grimme, Chem. Ber. 98, 756 (1965).
3. W. R. Roth, Ann. 671, 10 (1964).
4. G. Ohloff, Chem. Ber., 93, 2673 (1960).
5. W. R. Roth and J. König, Ann. 688, 28 (1965).
6. R. J. Ellis and H. M. Frey, Proc. Chem. Soc., 221 (1964); N. M. Frey, Adv. Phys. Org. Chem., 4, 147 (1966).
7. The preparation of 2-4 will be dealt with in a separate account on the photochemistry of these esters. The spectral properties have been reported [M. J. Jorgenson and T. Leung, J. Am. Chem. Soc., 90, 3769 (1968)].
8. Isomer 4c had characteristic olefinic hydrogen absorption in the nmr at 4.02τ; the corresponding absorptions for 4a and 4b were at 3.65 and 4.50τ, respectively, that of the fourth isomer at 4.83τ.
9. C. Walling and W. Thaler, J. Am. Chem. Soc., 83, 3877 (1961); P. D. Bartlett, L. K. Montgomery and B. Seidel, ibid., 86, 616 (1964).
10. R. Hoffman, J. Am. Chem. Soc., 90, 1475 (1968) and references therein. J. A. Berson and J. M. Balquist, ibid., 90, 7343 (1968); W. L. Carter and R. G. Bergman, ibid., 90, 7344 (1968).
11. The further possibility that in cis esters 2b, 3b and 4b the transformation to diene takes place via a 1,7 hydrogen shift is not considered here.