The Thermolysis of 2,2-Dimethyl-1-vinylcyclobutane

James S. Chickos and H. Monty Frey,*
Department of Chemistry, University of Reading, Whiteknights, P. O. Box 224, Reading RG6 2AD

The kinetics of the thermolysis of 2,2-dimethyl-1-vinylcyclobutane have been investigated as a function of temperature from 263 to 301 °C. Primary products produced in the reaction include isobutene and butadiene, 4,4-dimethylcyclohexene, 2-methylhepta-1,6-diene, and *cis*-2-methylhepta-1,5-diene. *trans*-2-Methylhepta-1,5-diene and 2,4-dimethylhexa-1,5-diene are produced from *cis*-2-methylhepta-1,5-diene by way of a 3,3-sigmatropic rearrangement. The reaction obeys first-order kinetics and is unaffected by surface. Activation energies (kcal mol^{-1}) and ($\log A/s^{-1}$) for the overall decomposition and for formation of the primary products are 45.73 ± 0.3 (14.427 ± 0.12), 47.71 ± 0.7 (15.087 ± 0.3), 44.35 ± 1.6 (12.53 ± 0.6), 45.0 ± 1.3 (12.24 ± 0.5), and 38.38 ± 1.7 (10.785 ± 0.7), respectively. The regiochemistry observed in fragmentation and in the 1,3-sigmatropic rearrangement of the starting material is discussed in terms of substituent effects found in other cyclobutane and vinylcyclobutane thermolyses. The fragmentation process and the isomerization to 4,4-dimethylcyclohexene and 2-methylhepta-1,6-diene is believed to proceed through the intervention of 6-methylhept-1-ene-3,6-diyl. *cis*-2-Methylhepta-1,5-diene is formed from a concerted 1,5-sigmatropic rearrangement of the starting material. The factors which affect the stereochemistry of the 1,5-hydrogen shift are discussed.

The thermolysis reactions of vinylcyclobutane and its derivatives offer a unique opportunity to examine how structure and stereochemistry affect the competition between various pathways. These pathways include the 1,3-sigmatropic rearrangements of carbon, the 2 + 2 cycloreversion reaction of the cyclobutane ring, and the 1,5-sigmatropic shifts of hydrogen observed in certain alkyl-substituted derivatives.

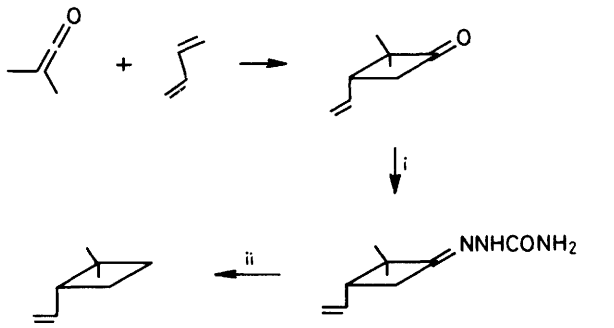
Very few kinetic studies have been reported on the effects of alkyl substitution on the parent system[1] although several stereochemical studies, *e.g.* those on *cis*- and (1*R*,2*S*)-*trans*-2-ethyl-1-vinylcyclobutane, *cis*- and *trans*-2-methyl-1-(*trans*-prop-1-enyl)cyclobutane, and *cis*- and *trans*-2-methyl-1-(*cis*-prop-1-enyl)cyclobutane, have appeared.[2,3] These studies, while offering significant stereochemical insight into the mechanisms of these rearrangements, are kinetically complicated by the *cis*–*trans* equilibration of the starting material which accompanies rearrangement. We report here the results of a kinetic study on 2,2-dimethyl-1-vinylcyclobutane, which, uncomplicated by geometrical isomerism, permits a direct and simple kinetic analysis of the products.

Recently, the gas-phase thermolysis of a close relative of 2,2-dimethyl-1-vinylcyclobutane, that of isotopically and stereochemically labelled α-pinene, has been reported.[4] The results, notably the conformational restraints introduced as a result of the bicyclic structure of α-pinene, offer an interesting comparison of the effects of structure on the fundamental processes which are found to compete in the thermal chemistry of these two compounds.

Experimental

2,2-Dimethyl-1-vinylcyclobutane was prepared according to Scheme 1 and characterised by its spectroscopic properties and its authenticity was confirmed by the nature of the products formed in its subsequent pyrolysis.

2,2-*Dimethyl*-3-*vinylcyclobutanone*.—The cyclobutanone was prepared from the cycloaddition of butadiene to dimethylketene as previously described.[5] Dimethylketene was prepared by subliming 2,2,4,4,tetramethylcyclobutane-1,3-dione through a quartz tube at 600 °C. The cycloaddition was carried out on a preparative scale by heating sealed thick-wall Pyrex tubes containing dimethylketene (1 ml) and butadiene (10 ml) at



Scheme 1. *Reagents:* i, $NH_2NHCONH_2$–CH_3CO_2Na; ii, Na–$(HOCH_2CH_2)_2O$

100 °C for 30 min. Combining the contents of several tubes and allowing the butadiene to evaporate afforded a mixture of liquid 2,2-dimethyl-3-vinylcyclobutanone and crystalline 2,2,4,4-tetramethylcyclobutane-1,3-dione. Decantation followed by vacuum distillation afforded 2,2-dimethyl-3-vinylcyclobutanone, b.p. 65—69 °C (35 mmHg) (lit.,[6] 91 °C at 100 mmHg); 3.4 g isolated from *ca.* 10 ml of dimethylketene; δ (60 MHz; neat liquid) 1.03 (s, 3 H), 1.17 (s, 3 H), 2.87 (m, 3.2 H), 5.1 (m, 2.1 H), and 5.97 (m, 1.1 H); $\nu_{max.}$(neat) 1 760 and 1 680 cm^{-1}.

2,2-*Dimethyl*-1-*vinylcyclobutane*.—2,2-Dimethyl-3-vinylcyclobutanone (3.4 g) was combined with semicarbazide hydrochloride (4.18 g), and sodium acetate (6.28 g) in water (50 ml)–alcohol (10 ml) and warmed. The crystalline semicarbazide formed immediately (5.5 g), m.p. 184—186 °C (lit.,[6] 188—189 °C).

A solution of sodium (1.2 g) and diethylene glycol (practical grade) was prepared in a round-bottom flask attached through an air condenser to a dry ice–acetone trap and maintained in a flow of nitrogen. The solution was heated and the semicarbazide (1 g) was added at an oil-bath temperature of 110 °C. The temperature was then rapidly raised to 210 °C and maintained for 1 h as previously described.[7] Frothing and gas evolution was evident at *ca.* 180 °C. 2,2-Dimethyl-1-vinylcyclobutane (0.2 g) was isolated in the dry ice trap and appeared to be *ca.* 90% pure. 2,2-Dimethyl-1-vinylcyclobutane (99 + %) was obtained by

preparative gas chromatography on a squalane column, δ (220 MHz; $CDCl_3$; Me_4Si) 0.96 (s, 3 H), 1.06 (s, 3 H), 1.74 (m, 4.1 H), 2.57 (q, 1.0 H), 4.94 (m, 2.0 H), and 5.86 (m, 1.03 H); $\nu_{max.}$ (*gas phase*; 30 mmHg) 1 640, 1 000, and 920 cm^{-1}; *m/e* 110 (M^+); major fragments at *P*–15, *P*–28; *P*–43; *P*–54, and *P*–56.

Thermolysis.—The thermolysis of 2,2-dimethyl-1-vinylcyclobutane was performed over the temperature range 262—301 °C in a conventional high-vacuum 'static' apparatus at a total pressure of *ca.* 3.3 kPa. Sample pressures in the thermolysis vessel were *ca.* 83 Pa, with the difference in pressure being made up by nitrogen gas. Sample transfer was achieved by sharing the contents of the reaction vessel with an evacuated glass vessel. Analysis of the reaction products was achieved by g.l.c. using a gas inlet system on 5% triscyanoethoxypropane (Chromosorb P)–oxydipropiononitrile columns in tandem ($\frac{1}{8}$ in × 11 ft; $\frac{1}{8}$ in × 12 ft, respectively) at 40 °C. The output of the f.i.d. was connected to a Hewlett–Packard 3380S integrator. Seven products in yields in excess of 0.5% could be resolved by the g.l.c. columns used. Eluted in order of increasing retention time were: isobutene and butadiene (in equal amounts), 2,2-dimethyl-1-vinylcyclobutane, 2,4-dimethylhexa-1,5-diene,* 4,4-dimethylcyclohexene (Aldrich), 2-methylhepta-1,6-diene,[8,†] *trans*-2-methylhepta-1,5-diene,‡ and *cis*-2-methylhepta-1,5-diene.‡

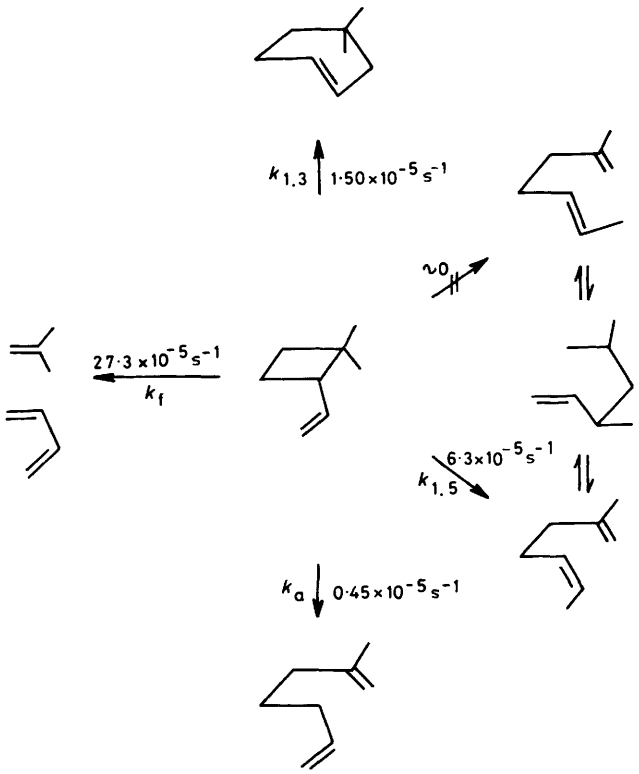
Analysis with a 4 m Porapak T column (120 °C) indicated <0.2% ethylene was present. Similarly, analysis for 3,3-dimethylcyclohexene (by comparison of retention times) using a synthetically prepared sample[9] showed none present to within the detection limit of the g.l.c. apparatus.

Product analysis was achieved by comparison of retention times with authentic samples and by co-injection on the analytical system described above, on squalane and bismethoxyethyl adipate columns. Thermolysis of 2,2-dimethyl-1-vinylcyclobutane using cyclohexane as an internal standard for various time intervals resulted in an analysis of cyclohexane that remained constant to within 1%. This result was interpreted to mean that mass balance for the reaction was complete and that the output of the flame ionization detector was proportional to carbon count. All products with the exception of *cis*-2-methylhepta-1,5-diene, as noted, were stable to the reaction conditions.

Parallel series of runs were conducted at 287.6 °C in an unpacked and packed reaction vessel (glass tubes) differing in surface-to-volume ratio by a factor >10. Least-squares fit of the data for the packed vessel for decomposition of starting material gave k_d 3.93 × 10^{-4} s^{-1}; intercept 0.999; correlation coefficient 0.999 98. Results obtained in the unpacked vessel were k_d 4.05 × 10^{-4}; intercept 0.982; correlation coefficient 0.9997.

Results and Discussion

The thermolysis of 2,2-dimethyl-1-vinylcyclobutane was studied in a Pyrex vessel from 262 to 301 °C. Thermolysis produced the products outlined in Scheme 2 and the kinetic data are summarized in Tables 1 and 2. The reaction obeyed first-order kinetics over the decomposition range studied which was generally for two half-lives. In addition since there was no significant effect of surface: volume ratio of the reaction vessel on the rate, there can be no appreciable heterogeneous component of the reaction.



Scheme 2. Thermal reactions of 2,2-dimethyl-1-vinylcyclobutane. $k_d = k_f + k_a + k_{1.3} + k_{1.5} = 35.6 \times 10^{-5}$ s^{-1} at 280 °C

Conspicuously absent in Scheme 2 is a fragmentation process to produce ethylene and 1,1-dimethylbutadiene. 3,3-Dimethylcyclohexene arising from a 1,3-sigmatropic rearrangement of the least substituted allylic bond was also shown to be absent. These results, which were obtained early in the study, prompted us to question the regiochemistry of the 2 + 2 cycloaddition reaction of dimethylketene with butadiene. Additional spectral studies of the reactant and structural assignments of the products, however, confirmed the assigned regiochemistry. Although the thermal reactions do not occur, fragmentation to produce ethylene and dimethylbutadiene as radical cations are important processes in the mass spectrum. Subsequent identification of *cis*- and *trans*-2-methylhepta-1,5-diene and 2-methylhepta-1,6-diene as important products in the reaction likewise are only compatible with the regiochemistry previously assigned in the cycloaddition reaction.[5,6]

Examination of the effect of alkyl substitution on the regiochemistry of cyclobutane fragmentation provides a rationale for the observed regiospecific fragmentation observed in 1,2-dimethylvinylcyclobutane. The data in Table 3 clearly demonstrate how regiochemistry in cyclobutane fragmentation is affected by both the number and stereochemistry of alkyl substitution. Increasing the number of vicinal alkyl groups increases the regioselectivity of fragmentation. The regiochemistry appears to be even more sensitive to vinyl group substitution as illustrated by the comparisons of the effects of methyl substitutions on the regioselectivity of fragmentation on the first three and last three entries in Table 3. The trends observed in Table 4 on the effects of methyl substitution on the regioselectivity of the vinylcyclobutane–cyclohexene rearrangement offer a similar explanation for the absence of 3,3-dimethylcyclohexene in the reaction products. *trans*-2-Methyl-1-vinylcyclopropane[10,11] as well as other vinylcyclopropanes[12]

* Prepared by heating a commercial sample of *cis*- and *trans*-2-methylhepta-1,6-diene in the reaction conditions.

† We thank Professor N. Lehnkuhl, Max-Planck-Institut Für Kohlenforschung, for kindly supplying us with a sample of 2-methylhepta-1,6-diene.

‡ Purchased as a *cis–trans* mixture (93% *trans*, 7% *cis*) from K and K Laboratories. The *trans*-isomer was identified by its shorter retention time on g.l.c. and its predominance in thermal equilibration studies.

Table 1. Rate constants for the decomposition of 2,2-dimethyl-1-vinylcyclobutane

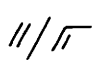
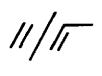
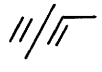
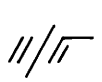
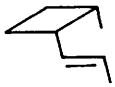
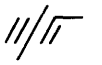
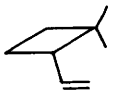
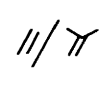
Temperature (°C)	262.8	269.0	275.5	279.2	287.65	294.1	301.1
$10^5\ k_d/s^{-1}$	5.91	9.91	16.5	21.3	40.5	62.8	106
$10^5\ k_f/s^{-1}$	4.41	7.31	12.0	16.5	32.5	48.4	84.2
$10^5\ k_a/s^{-1}$	0.0768	0.132	0.231	0.266	0.445	0.867	1.35
$10^5\ k_{1,3}/s^{-1}$	0.285	0.455	0.795	0.909	1.60	2.96	4.66
$10^5\ k_{1,5}/s^{-1}$	1.44	1.98	3.43	3.62	5.93	10.6	15.8

Table 2. Arrhenius activation energies for the thermal decomposition of 2,2-dimethyl-1-vinylcyclobutane

$\log (k_d/s^{-1}) = (14.427 \pm 0.12) - (45\,730 \pm 300)$ cal mol^{-1}/RTln10
$\log (k_f/s^{-1}) = (15.087 \pm 0.3) - (47\,714 \pm 700)$ cal mol^{-1}/RTln10
$\log (k_a/s^{-1}) = (12.244 \pm 0.6) - (45\,000 \pm 1\,300)$ cal mol^{-1}/RTln10
$\log (k_{1,3}/s^{-1}) = (12.53 \pm 0.5) - (44\,400 \pm 1\,200)$ cal mol^{-1}/RTln10
$\log (k_{1,5}/s^{-1}) = (10.80 \pm 0.7) - (38\,380 \pm 1\,700)$ cal mol^{-1}/RTln10

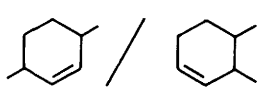
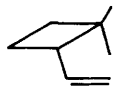
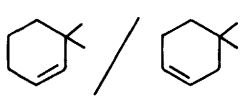
Errors reported are one standard deviation.

Table 3. The effect of alkyl substitution on the regiochemistry of fragmentation of various cyclobutanes at 286 °C

Cyclobutane	Olefin		Ref.
		1/4·8 [a]	b
		1/8·4 [a]	b
		1/15 [a]	c
		1/6·1	2,3
		1/22	2,3
		~0	This work

[a] Obtained by extrapolation of the activation parameters to 286 °C. [b] H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, 1961, **83**, 4884. [c] A. T. Cocks and H. M. Frey, *J. Phys. Chem.*, 1971, **75**, 1437.

Table 4. Effects of alkyl substitution on the regiochemistry of some 1,3-sigmatropic rearrangements at 286 °C

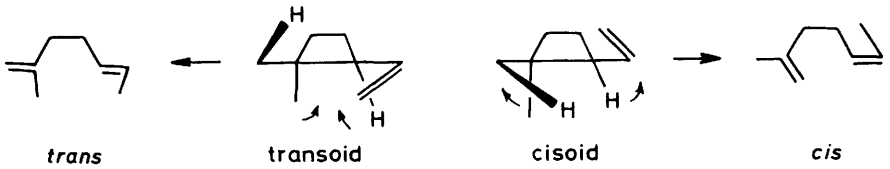
Reactant	Olefin ratio	Ref.
	 1/6·3	2,3
	 ~0	2,3
	 ~0	This work
	 ~0	10[a]

[a] H. M. Frey and R. K. Solly, *Int. J. Chem. Kinet.*, 1969, **1**, 473.

exhibit similar regiochemistry in their 1,3-sigmatropic rearrangements.

cis-2-Methylhepta-1,5-diene, the product derived from a 1,5-sigmatropic migration of hydrogen in 2,2-dimethyl-1-vinylcyclobutane, is the only 1,5-diene to appear early in the reaction. *trans*-2-Methylhepta-1,5-diene, which predominates at equilibrium, and 2,4-dimethylhexa-1,5-diene are not found initially in the thermolysis. Their ratio (4:1) was observed to remain reasonably constant during the course of reaction, while the ratio of *cis*-2-methylhepta-1,5-diene to 2,4-dimethyl-1,5-hexadiene was observed to vary from 40:1 to 4:1 during the course of decomposition of the starting material. 2,4-Dimethylhexa-1,5-diene is rapidly formed from a commercial sample of *trans*- and *cis*-2-methylhepta-1,5-diene under the experimental conditions. Differences observed in the rate of equilibration of *cis*- and *trans*-2-methylhepta-1,5-diene with 2,4-dimethylhexa-1,5-diene can be explained in terms of the transition state for the Cope rearrangement.[13] In the equilibration of *trans*-2-methylhepta-1,5-diene with 2,4-dimethylhexa-1,5-diene, both methyl groups can be accommodated in equatorial positions in the chair-like transition state necessary for rearrangement. In the equilibration of the *cis*-isomer with 2,4-dimethylhexa-1,5-diene, one methyl group must be forced into an axial position resulting in a subsequent retardation of this process.

Rearrangement by way of a 1,5-sigmatropic hydrogen shift accounts for 18% of the reaction of 2,2-dimethyl-1-vinylcyclobutane at 286 °C. Similar rearrangement results reported for other *cis*-substituted vinylcyclobutanes and vinylcyclopropanes are included for comparison in Table 5. With the exception of the third entry in this Table, the relative importance of the 1,5-hydrogen shift is comparable for all vinylcyclobutane entries. As far as the product stereochemistry is concerned, our results for 2,2-dimethyl-1-vinylcyclobutane are the same as those obtained from the alkylvinylcyclopropanes. Only the *cis*-olefin is obtained. The *trans*-olefin reported for entries 2—4 in Table 5 may in fact be a secondary product arising from a 3,3-sigmatropic rearrangement of the *cis*-olefin similar to what we have observed for *cis*-2-methylhepta-1,5-diene.[2] A rationale for the formation of only the *cis*-isomer in these systems can be obtained by an examination of the transition state for rearrangement. The rigidity imposed by the presence of the cyclopropane and cyclobutane rings is likely to force the six-atom cyclic transition state for the 1,5-sigmatropic shift into a cyclohexene-like chair conformation as shown in Scheme 3 for 2,2-dimethyl-1-vinylcyclobutane. Opening of the cyclobutane ring can occur either in a disrotatory or conrotatory mode.

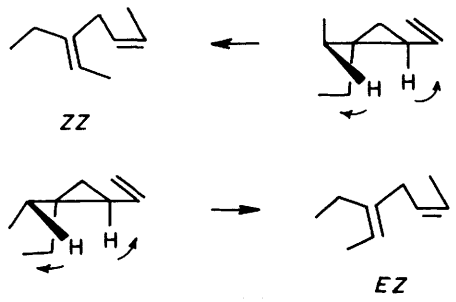


Scheme 3.

Models show that maximum overlap and least motion between the σ and *p* orbitals involved in the rearrangement can best be maintained by disrotatory opening of the cyclobutane ring. In the 'transoid' conformation, this is best achieved by moving the methyl and hydrogen substituents on the ring toward each other while in the 'cisoid' conformation the relative motions of these two groups must be reversed to maximize this overlap. It is presumably the lack of substituent interaction in this latter case which controls the stereochemistry of the olefin formed. In addition, models indicate that disrotatory ring opening of the 'transoid' form in which the methyl and hydrogen groups move towards each other actually forces the vinyl group to move away from the hydrogen which is being transferred. Such an effect is not observed in the disrotory least motion-maximum overlap ring opening of the 'cisoid' conformation.

Conrotatory ring opening of the cyclobutane ring leads directly to a situation where the *p* orbitals of one of the two double bonds in the products approach orthogonal rather than parallel arrangements. This situation is a consequence of conrotation in both the 'cisoid' and 'transoid' conformations and would be expected to result in a higher energy process.

The report that thermolysis of 2,2-diethyl-1-vinylcyclopropane gives slightly more 3-ethylhepta-2*E*,5*Z*-diene (0.51) than the corresponding 2*Z*,5*Z*-isomer (0.49) offers some support for the notion that the transition state for 1,5-hydrogen transfer proceeds through a cyclohexene-like chair conformation. The observed stereochemistry is explained by the preference of the methyl group to occupy a pseudo-equatorial rather than pseudo-axial position in the transition state as shown in Scheme 4. This preference however is small. The effect of a *cis*-propenyl



Scheme 4.

group in retarding the 1,5-sigmatropic rearrangement in *cis*-2-methylprop-1-enylvinylcyclobutanes shown in Table 5 is also readily understood in terms of the proposed transition state for rearrangement. The *cis*-methyl group in the prop-1-enyl group is forced to occupy a pseudo-axial position in the transition state and this results in additional non-bonded interactions with the methylene groups of the cyclobutane ring. This reduces the importance of the 1,5-hydrogen-shift reaction in this compound relative to the *trans*-isomer in which the methyl group can be accommodated in a pseudo-equatorial position.

A boat-like transition state is also possible for explaining the 1,5-hydrogen shift in 2,2-dimethyl-1-vinylcyclobutane. In this instance, least motion-maximum overlap considerations predict conrotatory opening of the cyclobutane ring accompanying the 1,5-hydrogen transfer as shown in Scheme 5.

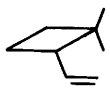
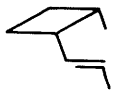
The presence of non-bonded interactions which destabilize the boat form of cyclohexane and increase the transition-state energy of the boat form in 3,3-sigmatropic rearrangements[13] is likely to destabilize the boat form in the 1,5-hydrogen transfer as well.[4] In addition, the boat-like transition state for the 1,5-hydrogen shift in 2,2-diethyl-1-vinylcyclopropane predicts preferential formation of 3-ethylhepta-2*Z*,5*Z*-diene. Although the stereochemical effects are small, this is contrary to what is observed experimentally.

Scheme 5.

2-Methylhepta-1,6-diene, which appears as a primary product in the thermolysis, can be viewed as being formed by a 1,5-hydrogen-abstraction reaction of the diradical. Cleavage of the most highly substituted allylic bond produces a diradical which can fragment to olefins, isomerize to a cyclohexene, or be trapped by hydrogen abstraction. Intramolecular hydrogen abstraction in a diradical formed from a cyclobutane, although rare, has previously been observed in the thermal decomposition of 1,1,3,3-tetramethylcyclobutane.[14] 2,4,4-Trimethylpent-1-ene is presumably formed from a similar 1,5-hydrogen shift in 2,2,4-trimethylpenta-1,4-diyl. A similar product also seems to have been observed in methylcyclobutane thermolysis.[14] All three hydrogen-abstraction products seem to be produced in comparable amounts, 1—3%.

Activation parameters have previously been measured for the decompositions and isomerizations of vinylcyclobutane, isopropenylcyclobutane, and α-pinene. These results, along with some additional data on cyclobutane fragmentation and a summary of our own results, are included in Table 6. Using activation parameters for fragmentation of *cis*- and *trans*-1,2-dimethylcyclobutane relative to cyclobutane as a measure of the *cis*- and *trans*-1,2-methyl interaction in trimethylcyclobutane, results in the prediction that 1,1,2-trimethylcyclobutane should fragment with a free energy of activation [$\Delta G^{\ddagger}$(286 °C)] of roughly 2.2 kcal mol^{-1} lower than cyclobutane. This is presumably due to the relief of non-bonded methyl–methyl interactions present in the ground state. Experimentally a value of 2.7 kcal mol^{-1} is observed. If the fragmentation of vinylcyclobutane proceeds through the same mechanistic profile as cyclobutane thermolysis, geminal dimethyl substitution at position 2 should cause a similar effect on the free energy of activation of vinylcyclobutane. Comparison of the $\Delta G^{\ddagger}$(298 °C) values in Table 6 shows a difference of 3.6 kcal mol^{-1} for 2,2-dimethyl-1-vinylcyclobutane which is comparable to the value observed for 1,1,2-trimethylcyclobutane. The larger difference of 5.5 kcal mol^{-1} in $\Delta\Delta G^{\ddagger}$ (298 °C) observed for the fragmentation of α-pinene probably reflects differences in strain and non-bonded interactions in going from a bicyclic to an acyclic olefin. A much smaller difference in $\Delta\Delta G^{\ddagger}$ (286 °C) of 0.8 kcal mol^{-1} is observed in the formation of 4,4-dimethylcyclohexene and cyclohexene, the products of the 1,3-sigmatropic rearrangement.

Table 5. Comparisons of the importance of the 1,5-sigmatropic rearrangement in some *cis*-2-alkylvinylcycloalkanes

Vinylcycloalkane	Fraction of 1,5-H shift to overall reaction $k_{1,5}/k_d$		Olefin	Ref.
		0.18	*cis*	This work
		0.27 (0.39)[a]	*cis, trans*	2,3
		0.03 (0.04)[a]	*cis, trans*	2,3
		0.65 (0.75)[a]	*cis, trans*	2,3
		1.0	*cis*	10[b]
		1.0	*cis*	11,13
		1.0	2*E*,5*Z* 2*Z*,5*Z*	*c*

[a] Ignoring geometric isomerization of the cyclobutane ring. [b] H. M. Frey and R. K. Solly, *Int. J. Chem. Kinet.*, 1969, **1**, 473. [c] H. M. Frey and R. K. Solly, *J. Chem. Soc. B*, 1970, 996.

However, this value is still within experimental error of the 3.6 kcal mol^{-1} difference observed in the fragmentation reaction. The 1,3-sigmatropic rearrangement of α-pinene remains consistently larger at 5.1 kcal mol^{-1} and probably reflects a greater relief of non-bonded interactions in the activated complex relative to the ground state of this molecule. Combination of the activation enthalpy for the 1,3-sigmatropic rearrangement (43.3 ± 1.2 kcal mol^{-1}) in 2,2-dimethyl-1-vinylcyclobutane with the allylic resonance energy (13 ± 1 kcal mol^{-1}), and the effect of alkyl substitution on the activation enthalpy (*ca.* 2.7 ± 1 kcal mol^{-1}), results in a value of 59 ± 2.5 kcal mol^{-1} which compares to $\Delta H^{\ddagger}$(286) of 61 kcal mol^{-1} for cyclobutane fragmentation. Such a treatment indicates the absence of a significant discrepancy between estimated and observed activation enthalpies and deprives the 1,3-sigmatropic rearrangement of an energetic basis for concert. A similar conclusion has been reached based on stereochemical and isotope effect studies.[2–4]

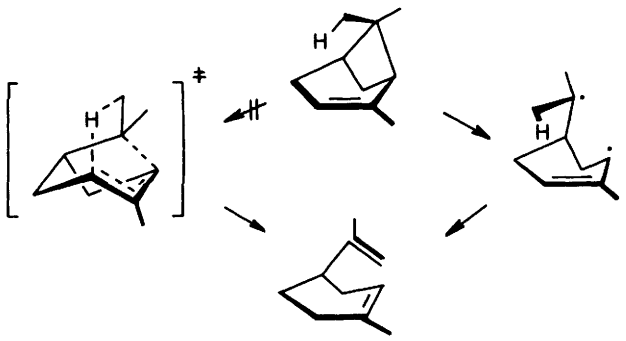
The 1,5-sigmatropic rearrangement of 2,2-dimethyl-1-vinylcyclobutane is the only process which exhibits activation parameters consistent with and characteristic of a concerted process. In this respect, *cis*-2-alkylvinylcyclobutanes parallel the behaviour of *cis*-2-alkylvinylcyclopropanes capable of a 1,5-hydrogen shift. Comparison of the activation energies for *cis*-2-methylvinylcyclopropane, E_a 31.2 kcal mol^{-1} (log A/s^{-1} 11.03), 2,2-dimethylvinylcyclopropane, E_a 33.5 (log A/s^{-1} 11.4), and 2,2-diethylvinylcyclopropane, E_a 33.72, 33.62 kcal mol^{-1} (log A/s^{-1} 11.31, 11.26 respectively)[15] to the results obtained here reveals an energy bias of roughly 5 kcal mol^{-1} for the 1,5-sigmatropic rearrangement in the cyclopropyl system. Although both systems are equally driven by relief of ring strain, the kinetic advantage exhibited by the cyclopropyl system is substantial and probably related to the effectiveness with which the cyclopropyl group conjugates to the reaction termini.[16] A similar kinetic effect has been observed in the concerted 3,3-sigmatropic rearrangement of *cis*-1,2-divinylcyclopropane and *cis*-1,2-divinylcyclobutane.[17]

The 1,5-sigmatropic rearrangement of 2,2-dimethyl-1-vinylcyclobutane, which appears on energetic grounds to be concerted, can be compared to results obtained on α-pinene. Kinetic as well as isotope effect studies provide compelling evidence that the 1,5-sigmatropic rearrangement in α-pinene occurs through an intermediate and is not concerted.[4] Unlike 2,2-dimethyl-1-vinylcyclobutane the concerted 1,5-hydrogen

Table 6. Activation parameters for cyclobutane thermolysis

Compound	Process	Products	log (A/s^{-1})	E_a/kcal mol^{-1}	$\Delta G^{\ddagger}$ (286 °C)/kcal mol^{-1}	Ref.
Cyclobutane	k_f	Ethylene	15.62	62.5	56.0	*a*
cis-1,2-Dimethylcyclobutane	k_f	Propene	15.48	60.4	54.2	*b*
trans-1,2-Dimethylcyclobutane	k_f	Propene	15.45	61.6	55.5	*b*
1,1,2-Trimethylcyclobutane	k_f	Ethylene + isobutene	15.78	60.2	53.3	*c*
Vinylcyclobutane	k_f	Ethylene + butadiene	14.87	50.7	46.1	1
	$k_{1,3}$	Cyclohexene	13.86	48.6	46.6	1
Isopropenylcyclobutane	k_f	Ethylene + 2-methylbutadiene	15.22	52.35	46.8	1
	$k_{1,3}$	1-Methylcyclohexene	13.76	48.95	47.2	1
(*S*)-α-Pinene	k_f	(*Z*)-2,6-Dimethylocta-2,5,7-triene	14.4	44.0	40.6	4
	$k_{1,5}$	Dipentene	13.7	42.0	40.4	4
	$k_{1,3}$	(*R*,*S*)-α-Pinene	14.5	45.2	41.5	4
2,2-Dimethyl-1-vinylcyclobutane	k_f	Ethylene + butadiene	15.09	47.71	42.5	This work
	$k_{1,3}$	4,4-Dimethylcyclohexene	12.53	44.4	45.8	This work
	$k_{1,5}$	2-Methylhepta-1,5-diene	10.8	38.38	44.2	This work
	k_a	2-Methylhepta-1,6-diene	12.24	45.0	47.1	This work

[a] C. T. Genaux and W. D. Walters, *J. Am. Chem. Soc.*, 1951, **73**, 4497; R. W. Carr and W. D. Walters, *J. Phys. Chem.*, 1963, **67**, 1370. [b] H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, 1961, **83**, 4884. [c] A. T. Cocks and H. M. Frey, *J. Phys. Chem.*, 1971, **75**, 1437.



Scheme 6.

shift in α-pinene is confined to a boat-like transition state because of geometrical constraints.

It is not clear to what extent the boat-like transition state is responsible for destabilizing the concerted 1,5-shift but this and presumably the additional strain involved in forming a tricyclic transition state combine to increase the activation enthalpy by >6 kcal mol^{-1}. Thus, despite a geometry which is predisposed to a concerted 1,5-shift, the favourable entropy factor is more than offset by unfavourable enthalpic factors. These results, while totally consistent with those obtained in this study, reinforce the importance of the chair-like transition state in the concerted 1,5-sigmatropic hydrogen shift such as observed in *cis*-2-alkylvinyl-cyclopropanes and -cyclobutanes.

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