

1068. The Thermal Unimolecular Isomerizations of *cis*- and *trans*-1-Methyl-2-vinylcyclopropanes.

By R. J. ELLIS and H. M. FREY.

The thermal isomerization of *cis*- and *trans*-1-methyl-2-vinylcyclopropanes have been studied in the gas phase. In the temperature range 166–220°, *cis*-1-methyl-2-vinylcyclopropane isomerizes to give *cis*-hexa-1,4-diene. This reaction is almost certainly unimolecular and the rate constants are fitted by the Arrhenius equation:

$$k = 10^{11.03} \exp(-31,240/RT) \text{ sec.}^{-1}$$

The reaction probably involves a 1,5-hydrogen shift in a seven-membered-ring transition complex.

trans-1-Methyl-2-vinylcyclopropane isomerizes by two parallel paths to yield *cis*-hexa-1,4-diene and 3-methylcyclopentene in the temperature range 296–328°. The ratio of the diene to the cyclopentene is 11.7:1 at all temperatures in this range. Both processes are also almost certainly unimolecular. The Arrhenius equations for these processes are:

$$k(\text{cis-diene}) = 10^{14.74} \exp(-48,640/RT) \text{ sec.}^{-1}$$

$$k(\text{cyclopentene}) = 10^{13.67} \exp(-48,640/RT) \text{ sec.}^{-1}$$

The energy of activation for the isomerization of the *trans*-cyclopropane to the *cis*-diene is thought to correspond to the energy required for the *trans*-*cis*-isomerization of the cyclopropane. Comparison of the value obtained in this work with that for the *trans*-*cis*-isomerization of 1,2-dimethylcyclopropane yields a value for the resonance energy of the allyl radical of 11.9 ± 1 kcal.

The rate constants for the reactions were independent of pressure in the range 3–40 mm. and also independent of the surface:volume ratio of the reaction vessel.

The construction of a precision high-temperature thermostat, employing a fused salt as the thermostat liquid, is described.

APPROPRIATELY substituted cyclopropanes^{1,2} are known to undergo reversible *cis*-*trans*-isomerizations which are almost certainly unimolecular. In addition, slower structural isomerizations occur to yield olefins. Vinylcyclopropanes³⁻⁵ undergo isomerizations to yield cyclopentenenes at rates considerably greater than the other cyclopropane isomerizations. The difference in rates is due to a much lower energy of activation for the reactions of the vinyl-substituted compounds. This has been ascribed to the effect of the delocalisational energy of the allyl radical in the transition state. Some difficulties of detailed interpretation of these differences have arisen owing to the possibility that the cyclopentene isomerization reaction occurs by a concerted mechanism involving a five-membered ring rather than a two-stage process involving the free diradical. The present work with the 1-methyl-2-vinylcyclopropanes was undertaken in an attempt to resolve this difficulty.

EXPERIMENTAL

Preparation of Materials.—The methylvinylcyclopropanes were prepared by the reaction of diazomethane in the presence of cuprous chloride on *cis*- and *trans*-penta-1,3-diene.

¹ B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, 1958, **28**, 504; E. W. Schlag and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996; H. M. Frey and D. C. Marshall, *J.*, 1963, **5717**; C. S. Elliott and H. M. Frey, *J.*, 1964, 900.

² M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122.

³ M. C. Flowers and H. M. Frey, *J.*, 1961, 3547.

⁴ H. M. Frey and D. C. Marshall, *J.*, 1962, 3981.

⁵ R. J. Ellis and H. M. Frey, *J.*, 1964, 959.

Purification of Commercial Penta-1,3-diene.—The commercial product was analysed by gas chromatography and found to consist of approximately 70% *trans*-penta-1,3-diene, 25% *cis*-penta-1,3-diene, and 5% cyclopentene. Pure *cis*-penta-1,3-diene was prepared from this mixture by the following procedure. The *trans*-isomer was removed by formation of the maleic anhydride adduct,⁶ the *cis*-isomer, together with the cyclopentene, being obtained by distillation from the pentadiene-maleic anhydride mixture. The *cis*-penta-1,3-diene and cyclopentene were treated with a large excess of cuprous chloride and ammonium chloride (resulting in the formation of a complex by the diene) and the cyclopentene was distilled off at room temperature. Finally, the diene complex was decomposed by heating at 100° to yield pure⁷ *cis*-penta-1,3-diene.

cis-1-Methyl-2-vinylcyclopropane was prepared by methylene addition to *cis*-penta-1,3-diene using the Gasper-Roth method.⁸ Dry diazomethane in a stream of nitrogen was passed into about 100 ml. of dry *cis*-penta-1,3-diene containing cuprous chloride (200 mg.). Preliminary experiments showed that the more substituted double bond was attacked first. However, once about 5% reaction had occurred, the rate of formation of methylvinylcyclopropane was equal to its rate of reaction with the diazomethane to yield methylbicyclopropane, thus indicating that the olefin is about 20 times more reactive than the diene towards the diazomethane-cuprous chloride reagent. Accordingly, the reaction was only allowed to proceed to a few percent to minimise the formation of the bicyclopropane. The unchanged penta-1,3-diene was removed by distillation and the residue fractionally distilled to yield a high- and a low-boiling fraction. The former consisted almost entirely of methylbicyclopropane. The low-boiling fraction consisted of *cis*-1-methyl-2-vinylcyclopropane with a small quantity of *cis*-1-cyclopropylbut-2-ene and some penta-1,3-diene. Pure *cis*-1-methyl-2-vinylcyclopropane was prepared from this fraction by gas chromatography using a column with dinonyl phthalate as the liquid phase. The resulting product was chromatographically pure. Mass-spectral analysis showed it to have a molecular weight of 82 with a cracking pattern consistent with it being methylvinylcyclopropane. The infrared spectrum was consistent with the compound being *cis*-1-methyl-2-vinylcyclopropane.

trans-1-Methyl-2-vinylcyclopropane was prepared directly from the commercial pentadiene by treatment with diazomethane and cuprous chloride. The cyclopropane was separated by fractional distillation, and a pure sample obtained from the crude distilled mixture by preparative gas chromatography using the dinonyl phthalate column. The product so obtained contained less than 0.5% total impurity. The infrared spectrum of the compound was consistent with it being *trans*-1-methyl-2-vinylcyclopropane.

Hexa-1,4-diene.—Allylacetone was reduced to hex-5-ene-2-ol using lithium aluminium hydride, and the alcohol was converted into its sodium salt using sodium hydride. This was converted into its xanthate, which was purified by distillation under reduced pressure. The xanthate was pyrolysed by dropping it into boiling diphenyl ether. The pyrolysis product was purified by distillation from sodium to yield a mixture of hexa-1,5-diene and *cis*- and *trans*-hexa-1,4-dienes. These compounds were separated by gas chromatography using a column with a liquid phase of di-(2-cyanoethyl) ether. The *cis*- and *trans*-isomers of the hexa-1,4-dienes were characterised by their infrared spectra.

3- and 4-Methylcyclopentenenes.—3-Methylcyclopentanone was reduced to the alcohol using lithium aluminium hydride. The alcohol was dehydrated using a drop of 50% phosphoric acid, and a mixture of 3- and 4-methylcyclopentenenes obtained by distillation. These were easily separable chromatographically.

Analysis.—The details of the analytical apparatus and the procedure employed have been reported previously.⁹ In studies with *cis*-1-methyl-2-vinylcyclopropane the analysis was carried out using a 12-ft. column containing 20% w/w of dinonyl phthalate on Chromosorb P. In studies with the *trans*-isomer the analysis was performed using two columns in series. The first was of 30 ft. containing 20% w/w di-(2-cyanoethyl) ether on Chromosorb P, followed by a 10-in. column containing 20% w/w of ethylene glycol saturated with silver nitrate on Chromosorb P. In both cases the analytical columns were operated at room temperature.

Apparatus.—A conventional high-vacuum static system was used. Greaseless stopcocks with Viton A diaphragms were employed throughout. In part of the work, pyrolyses were carried

⁶ D. Craig, *J. Amer. Chem. Soc.*, 1950, **72**, 1678; R. L. Frank, R. D. Emmich, and R. S. Johnson, *ibid.*, 1947, **69**, 2313.

⁷ D. Craig, *J. Amer. Chem. Soc.*, 1943, **65**, 1006.

⁸ W. von E. Doering and W. R. Roth, *Tetrahedron*, 1963, **19**, 729.

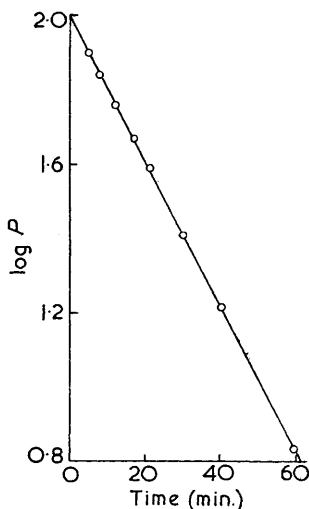
⁹ R. J. Ellis and H. M. Frey, *J.*, 1964, 4184.

out in a 200-ml. cylindrical Pyrex vessel mounted in a vertical air furnace¹⁰ controlled by a Sunvic RT2 regulator. However, at the relatively low temperatures required in this work it is very difficult to maintain the temperature constant and also to obtain uniformity of temperature over the volume of the reaction vessel, owing to the relatively long time-constant of the furnace. Accordingly, the majority of the runs was carried out with the vessel immersed in a fused-salt bath. This is essentially a high-temperature thermostat employing a fused-salt mixture (53% KNO₃, 47% NaNO₂) as the thermostat liquid. The fused salt was contained in a thin-walled aluminium beaker which was thermally insulated. The salt bath was heated by means of a 22-ft. stainless-steel sheathed heater wound spirally around the inside of the aluminium beaker. The temperature was controlled using an A.E.I., RT3R regulator, with a platinum resistance thermometer immersed in the fused salt as the sensing element. The fused salt was stirred by a 30-w Griffin and George motor fitted with a 4-blade (1 in.) stirrer. Temperatures were measured using a Pt/Pt-13%Rh thermocouple and a potentiometer. The temperature could be maintained to better than 0.1°, and the temperature gradient in the bath over the entire volume of the reaction vessel was also less than 0.1°. The top of the aluminium beaker was completely covered by four layers of ¼-in. Sandanyo board, each layer being separated by a ¼-in. air-gap. Connections to the vessel, resistance thermometer, thermocouple, and stirrer all passed through holes drilled through the Sandanyo "sandwich". The stirrer, aluminium can, and RT3R regulator were all provided with a common earth. The greaseless stopcock connecting the reaction vessel to the rest of the vacuum system was mounted immediately on top of the Sandanyo cover, thus producing a negligible dead-space.

Identification of Products.—Products from the pyrolyses were identified in the first instance by comparison of their retention times on the chromatographic columns with those of authentic samples. In cases of doubt different liquid phases were used for the columns. The major product, *cis*-hexa-1,4-diene, was further confirmed by trapping the relevant peak, after elution from the chromatograph and recording its infrared spectrum, using a micro-gas cell.

RESULTS

***cis*-1-Methyl-2-vinylcyclopropane.**—In the temperature range 166—222°, in an aged reaction vessel, *cis*-1-methyl-2-vinylcyclopropane isomerizes to yield *cis*-hexa-1,4-diene as the only product. The isomerization was strictly first-order, and a typical kinetic plot is shown in the Figure, where decomposition was taken to nearly 95% completion. Since the plot shows no curvature, it is fairly certain that the isomerization cannot be proceeding by a radical-chain path (since the product is a chain inhibitor, any such radical component would produce a higher initial rate).



Isomerization of *cis*-1-methyl-2-vinylcyclopropane at 208.7° (P = percentage of the cyclopropane).

¹⁰ H. M. Frey and R. C. Smith, *Trans. Faraday Soc.*, 1962, **58**, 697.

Rate constants were determined from plots of the type shown in the Figure by the method of least squares, at 10 different temperatures. The values obtained are shown in Table 1.

TABLE 1.

Rate constants for the isomerization of *cis*-1-methyl-2-vinylcyclopropane.

Temp. (°C)	166.2	181.2	181.9	195.7	208.7	222.1	174.3*	190.5*	201.3*	216.7*
10^4k (sec. ⁻¹)	0.334	0.985	1.07	2.84	7.42	17.5	0.62	2.13	4.58	13.5

* Results obtained using furnace.

An Arrhenius plot of all the rate constants gave a good straight line. However, the four values obtained using the furnace gave a slightly greater slope than those obtained in the fused-salt bath. The Arrhenius parameters corresponding to the two sets of data were evaluated by least squares, whence;

	<i>E</i> (kcal.)	$\log_{10} A$
Salt bath	31.24	11.029
Furnace	31.67	11.265

Owing to the greater precision with which the temperature could be controlled in the salt-bath we feel these results to be more reliable and accurate; hence, the preferred Arrhenius equation for the isomerization of *cis*-1-methyl-2-vinylcyclopropane is $k = 10^{11.03} \exp(-31,240/RT)$ sec.⁻¹.

A series of isomerizations was carried out at 216.7° in a cylindrical Pyrex vessel packed with open Pyrex tubes. The surface: volume ratio of this vessel was about 10 times greater than the unpacked vessel used in the remainder of the work. The rate constant obtained, *viz.*, 1.35×10^{-3} sec.⁻¹, was identical in both vessels. Hence, there can be no appreciable heterogeneous component of the reaction.

In the majority of runs the pressure was 3 mm. A few runs were carried out at various pressures in the range 3—40 mm. The rate constants were independent of pressure in this range.

trans-1-Methyl-2-vinylcyclopropane.—The isomerization of *trans*-1-methyl-2-vinylcyclopropane was investigated in the temperature range 296—328°. All pyrolyses were performed using the fused-salt bath. The major product was again *cis*-hexa-1,4-diene, but in this case another product, 3-methylcyclopent-1-ene, was formed in significant amounts. In addition, another product was formed in very minor quantities with a retention time very close to that of the 3-methylcyclopentene. The amounts of this compound were too small to allow positive identification. The overall rate constants for the isomerization of the *trans*-cyclopropane were determined by the same method used for the *cis*-compound. The values obtained are shown in Table 2.

TABLE 2.

Overall rate constants for isomerization of *trans*-1-methyl-2-vinylcyclopropane.

Temp. (°C)	296.9	302.5	309.7	315.5	321.3	327.9	328.2
10^4k (sec. ⁻¹)	1.35	2.08	3.45	5.23	7.80	12.5	12.7

The individual rate constants for the two parallel processes, k_1 and k_2 , were determined by plotting the yield of the hexadiene against $[1 - \exp(-kt)]$. From the slope at each temperature and the value of the overall rate constant the values of k_1 (*cis*-hexa-1,4-diene) were calculated. Since the values of the slopes of these plots were independent of temperature in the range covered, then, within experimental error, the two reaction paths must have the same energy of activation. The values for k_2 (3-methylcyclopentene) were determined by subtraction of the values of k_1 from the overall rate constants. The values for k_1 and k_2 are given in Table 3.

TABLE 3.

Rate constants for the two isomerization paths of *trans*-1-methyl-2-vinylcyclopropane.

Temp. (°C)	296.9	309.7	315.5	321.3	327.9	329.8
10^4k_1 (sec. ⁻¹)	1.245	3.176	4.821	7.185	11.48	11.66
10^4k_2 (sec. ⁻¹)	0.107	0.272	0.413	0.615	0.98	1.00

The values of k_1 gave an excellent Arrhenius plot from which the Arrhenius parameters were evaluated by the method of least squares. The ratio $k_1:k_2$ was 11.7:1 throughout the entire temperature range, so that this ratio must represent the ratio of the "A" factors for the two reaction paths. The rate equations obtained for the two processes are:

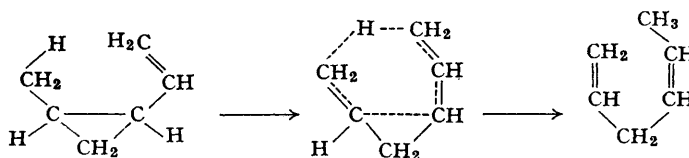
$$k_1 (\text{cis-hexa-1,4-diene}) = 10^{14.74} \exp(-48,640/RT) \text{ sec.}^{-1}$$

$$k_2 (3\text{-methylcyclopentene}) = 10^{13.67} \exp(-48,640/RT) \text{ sec.}^{-1}$$

Since the amounts of the methylcyclopentene were always small and since the chromatographic peak contained a contribution due to the unidentified minor product, the precision with which k_2 was determined was appreciably less than that with which k_1 was obtained.

DISCUSSION

The Arrhenius parameters for the isomerization of *cis*-1-methyl-2-vinylcyclopropane are considerably smaller than for any other reported isomerization of a cyclopropane. The product is also of a type not previously obtained in such an isomerization. The experimental evidence presented suggests, however, that, as in the other pyrolyses of cyclopropanes, the reaction is a true unimolecular transformation. The following transition state is suggested for this reaction.



The seven-membered-ring transition state is consistent with the low *A* factor for the reaction, which corresponds to a considerable loss of entropy in the transition complex ($\Delta S \sim -11.6$ e.u.). In this respect the reaction is unique for a cyclopropane isomerization, since in all other cases the entropy of activation is positive. The low energy of activation for the reaction is also explicable by the postulated mechanism, and indicates that the process of transferring the hydrogen atom and the breaking of the cyclopropane ring is concerted. It should be noted that the contribution to stabilization of the transition complex by allylic delocalization energy must be considerable. The only similar systems involving a 1,5-hydrogen-transfer mechanism that have so far been investigated in the gas phase are concerned with the thermal rearrangements of some 1,3-dienes.¹¹ Whilst energies of activation for such rearrangements have not yet been determined, it was found that the isomerization between 4-methylpenta-1,3-diene and *cis*-2-methylpenta-1,3-diene only proceeded at a measurable rate above 300°. In addition, since this rearrangement involves a six- rather than a seven-membered ring it is likely that the reaction has an *A* factor between 10 and 100 times greater than in the case of the methylvinylcyclopropane. This implies that, in the aliphatic case, the energy of activation must be considerably higher than the value of 31 kcal. obtained in this work. This difference is undoubtedly due to the assistance given to the formation of the transition complex by the relief of ring strain in the cyclopropane ring. Finally, the postulated mechanism accounts for the selective formation of only the *cis*-diene.

The isomerization of *trans*-1-methyl-2-vinylcyclopropane to *cis*-hexa-1,4-diene cannot proceed directly by a 1,5-hydrogen migration owing to the spatial configuration of the molecule. This isomerization almost certainly must proceed by the breaking of the 1,2-bond in the cyclopropane ring, followed by rotation to the *cis*-configuration. This *cis-trans*-isomerization of cyclopropanes is known to occur.^{1,2} At temperatures where this reaction occurs in the present system the lifetime of the *cis*-1-methyl-2-vinylcyclopropane resulting from this reaction would be too small for any to be detectable as a reaction product. Thus, the

¹¹ J. Wolinsky, B. Chollar, and M. D. Baird, *J. Amer. Chem. Soc.*, 1962, **84**, 2775.

Arrhenius parameters for the isomerization of the *trans*-cyclopropane to the *cis*-diene are, in fact, the values for the *cis-trans*-isomerization. It is not, of course, necessary for the ring-closure to occur, and it may well be that, once the 1,2-bond is broken and rotation occurs, the reaction gives the diene directly. However, since a cyclopropane ring broken in this fashion has, of necessity, sufficient energy to recyclise, the Arrhenius parameters will still be identical with those for the *cis-trans*-isomerization.

If the energy of activation obtained for the *trans*-methylvinylcyclopropane is compared with the value obtained for the *trans-cis*-isomerization of 1,2-dimethylcyclopropane, then the difference obtained, 11.9 ± 1 kcal., represents the contribution due to allylic resonance energy. In the past we have argued that the value of 13.2 ± 1 kcal. for the allylic resonance energy, obtained from considerations of the differences between the energy of activation for the isomerization of 1,1-dimethylcyclopropane to methylbutene and of 1-methyl-1-vinylcyclopropane to 1-methylcyclopentene, represents an underestimate of the total delocalization energy of this radical. We believed that the electron could not be completely delocalized, owing to steric requirements of the transition state. However, if the mechanism for the rearrangement is a concerted one, then, though the steric requirements of the complex will lead to a reduction in the available delocalization energy, this will be offset by a contribution due to the formation of the new carbon-carbon bond. It now appears that if the concerted mechanism is operative, then, quite fortuitously, the two effects approximately cancel one another. Alternatively, the completely free diradical may represent the transition complex, in which case the comparison leads to the allylic resonance energy directly. Whatever reaction path is accepted, the present work, which does not suffer from the same difficulties of interpretation, strengthens the evidence for a value for the allylic resonance energy of 11.9 kcal. This value is in excellent agreement with the value of 13.3 ± 1.3 kcal. obtained by Benson *et al.*¹³ and the more recent value of 12.6 ± 1 kcal. obtained by Egger, Golden, and Benson¹⁴ from studies of iodine-catalysed isomerizations of olefins. If these values are accepted then earlier estimates from more-complex systems^{15,16} are in error by approximately 100%. In addition, theoretical estimates appear also to be in error.¹⁷

The minor course of the isomerization of *trans*-1-methyl-2-vinylcyclopropane leads to 3-methylcyclopentene. This is exactly analogous to the isomerization of vinylcyclopropane^{1,12} and other substituted vinylcyclopropanes^{3,4} that have already been studied. The Arrhenius parameters are very similar to those obtained in these studies. The absence of any 4-methylcyclopentene is surprising, since it is to be expected that the transition state leading to the formation of this compound would have a slightly lower potential energy than that leading to the observed cyclopentene, since it involves the breaking of a slightly weaker carbon-carbon bond. We believe this may be evidence that, even in the isomerization leading to a cyclopentene, the transition complex does involve a completely free diradical. Under these circumstances, no 4-methylcyclopentene would be formed since, once the appropriate diradical is formed, the most probable reaction path would lead to *cis*-hexa-1,4-diene.

Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, SOUTHAMPTON.

[Received, August 19th, 1964.]

¹² C. A. Wellington, *J. Phys. Chem.*, 1962, **66**, 1671.

¹³ S. W. Benson, A. N. Bose, and P. Nangia, *J. Amer. Chem. Soc.*, 1963, **85**, 1388.

¹⁴ K. W. Egger, D. M. Golden, and S. W. Benson, personal communication.

¹⁵ M. Szwarc and A. H. Sehon, *J. Chem. Phys.*, 1950, **18**, 237.

¹⁶ A. S. Gordon, S. R. Smith, and J. R. McNesby, *J. Amer. Chem. Soc.*, 1959, **81**, 5059.

¹⁷ J. L. Franklin and F. H. Field, *J. Amer. Chem. Soc.*, 1953, **75**, 2819.