late (0.03 mol) in absolute benzene (50 ml). The mixture was refluxed overnight and the work-up was as described above.

Other Esters. Methyl phenylphosphinate (**4a**) was prepared from phenylphosphinyl chloride and sodium methoxide. Methyl methylphenylphosphinate (**4b**) was prepared from methylphenylphosphinyl chloride and $NaOCH_3$. Methyl diarylphosphinate esters (**6**) were prepared by the addition of diazomethane to the appropriate diarylphosphinic acid.

Rate Measurements. The solvents used were 33% dioxane–67% water (v/v) or 60% dimethoxyethane–40% water (v/v).[38] For slower reactions, a solution containing known amounts of ester and base was prepared at room temperature, thoroughly mixed, and placed in a constant-temperature bath. Sodium perchlorate was added where necessary to constant ionic strength. For faster rates, separate solutions of ester and base were prepared, brought to reaction temperature, and mixed. At appropriate time intervals, aliquots were removed and hydroxide ion titrated with standard perchloric acid; alternatively, the aliquot was quenched with perchloric acid and back-titrated with standard base to a pH of 8.45.

The titration volumes were related to concentrations of ester and base, and rate constants were obtained from both graphical analyses and computer programs utilizing a least-squares approach.[39,40] More detailed data are available.[1]

Analog Computation. In order to fit the data for hydrolysis of **5e** (Figure 1), a circuit corresponding to eq 2 was designed.[40] We fit the data for concentration of product as a function of time. The resistors were measured accurately when the fit was satisfactory, and it was shown that 5% errors in any of the resistors led to changes in the calculated curve exceeding error in the experimental curve.

Oxygen-18 Experiments. The reaction solutions were prepared using 1.8% ^{18}O-enriched water. The phosphinates isolated from enriched solvent were reisolated from solvent containing unenriched water to ensure freedom from ^{18}O contamination.

Phosphinates were analyzed for ^{18}O by conversion to CO_2 with a 1:1 mixture of $HgCl_2$–$Hg(CN)_2$ at 450°.[18,41] Water was equilibrated with CO_2 by the method of Cohn[42] and was also treated with $HgCl_2$–$Hg(CN)_2$ to give CO_2.[43,44] The CO_2 could be obtained in a nearly pure state by a trapping procedure previously described.[26,45] Complete mass spectra were taken to ensure the purity of the CO_2 sample. The reliability of the method was checked by control experiments using unlabeled materials. The accuracy of the mass spectrometer was checked regularly by determination of the oxygen-18 content of CO_2 from a cylinder kept for this purpose. On this particular spectrometer, it was found that 75 μ was the minimum CO_2 pressure required for consistent results.

Acknowledgment. Jean McNeal and Paul Ossip prepared some of the esters which were studied, and Arthur H. Fierman did the fit by analog computer to the data for hydrolysis of methyl diisopropylphosphinate. We thank Professors W. P. Jencks and M. M. Kreevoy for valuable discussions.

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(38) Both solvents were found suitable for these kinetic studies. However, in both media, acidic substances are formed by prolonged heating. Of the two solvents, dimethoxyethane was less prone to decomposition.

(39) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961; W. M. Youder, "Statistical Methods for Chemists," Wiley, New York, N. Y., 1961.

(40) F. D. Tabbutt, *J. Chem. Educ.*, **44**, 64 (1967).

(41) L. L. Berger and R. M. Wagner, *J. Chem. Eng. Data*, **3**, 310 (1958).

(42) S. Litthauer, *Chem. Ber.*, **22**, 2144 (1889).

(43) M. Anbar and S. Guttman, *Int. J. Appl. Radiat. Isotop.*, **4**, 233 (1959).

(44) M. Cohn, *Methods Enzymol.*, **4**, 905 (1957). The value of the equilibrium constant for $CO_2 + H_2{}^{18}O \rightleftarrows CO^{18}O + H_2O$ needed in this determination has been confirmed to be 2.09.[17]

(45) When the dialkylphosphinic acids were treated with HgCl alone,[46] many of the CO_2 samples were contaminated with ethylene. The purest samples of CO_2 were obtained when iodine was used to trap the ethylene. When diphenylphosphinic acid was heated with $HgCl_2$ alone[46] or with guanidine hydrochloride,[47] little or no CO_2 was obtained and, in the latter case, the CO_2 that was collected was badly contaminated with impurities.

(46) D. Rittenberg and L. Pontecorvo, *Int. J. Appl. Radiat. Isotop.*, **1**, 208 (1956).

(47) P. D. Boyer, D. J. Graves, C. H. Suelter, and M. E. Dempsey, *Anal. Chem.*, **33**, 1906 (1961).

Rates and Mechanisms in the Rearrangements of Vinylmethylenecyclopropane and Vinylethylidenecyclopropane[1]

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Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. *Received May 19, 1973*

Abstract: Vinylmethylenecyclopropane rearranges in the gas phase or in solution to give 3-methylenecyclopentene. The first-order rate constant in the gas phase is given by the expression $k = 10^{11.5}\exp(-26{,}000/RT)$. This activation energy is about the same as the lowest estimate of the energy of the 2,3 bond of the reagent, therefore not allowing an unequivocal choice between a diradical mechanism and a concerted process. In solution the activation energy is about the same, although the A factor is larger by a factor of 2. Vinylethylidenecyclopropane also rearranges. The two geometric isomers rearrange at different rates, each yielding a different mixture of 3-ethylidenecyclopentene and 3-methylene-4-methylcyclopentene. Two compounds appear transiently in the reaction of the faster isomer. They are identified as *cis*- and *trans*-3-methyl-2-vinyl-1-methylenecyclopropane. Rates of all interconversions have been studied, and [1,3]-sigmatropic shifts can alone account for all the products, although some [3,3] shifts are not excluded. Arguments favoring but not requiring concerted mechanisms are presented.

The facile rearrangement of vinylmethylenecyclopropane has been reported,[3] as have those of several of its derivatives.[4] The question of mechanism is

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(1) Some of this work was presented by title at the I.U.P.A.C. meeting, Boston, Mass., 1971. Another portion was presented by S. Vanderpool as a Student Affiliate Paper at the Southwest Regional Meeting of the American Chemical Society, San Antonio, Texas, 1971. In part from the Ph.D. Thesis of K. H. Leavell, Rice University, 1971. This work was supported by a grant (GP9603) from the National Science Foundation and by the Research Corporation. Acknowledgment is made to the donors of the Petroleum Research Fund (Grant No. 4828-AC1,4), administered by the American Chemical Society, for partial support. We thank Dr. G. P. Glass for help with the computer program.

(2) (a) Alfred P. Sloan Foundation Fellow, 1973–1975. (b) National Science Foundation Predoctoral Fellow.

(3) T. C. Shields, W. E. Billups, and A. R. Lepley, *J. Amer. Chem. Soc.*, **90**, 4749 (1968).

(4) (a) T. C. Shields and W. E. Billups, *Chem. Ind.* (*London*), 619 (1969); (b) W. E. Billups, K. H. Leavell, W. Y. Chow, and E. S. Lewis,

obscured by ambiguity about the fate of each reagent atom since the product can be formulated as either a [3,3] sigmatropic or Cope rearrangement, or as a [1,3] sigmatropic (or vinylcyclopropane rearrangement). There is also some question about whether the rearrangement is concerted or whether it passes through an intermediate diradical. We report here a study of the kinetics of the rearrangement of the parent molecule, and also of vinylethylidenecyclopropane, in which the ambiguity is removed by the methyl label.

The rearrangement of reaction 1 was followed in the


(1)

gas phase, using a diffusively stirred flow system with nitrogen as the carrier gas.[5] The reaction has the characteristics of a unimolecular reaction, with first-order kinetics, no detected side reactions, no apparent seasoning or surface effects, and no scatter characteristic of adventitiously initiated or inhibited chain reactions.

The results are shown as an Arrhenius plot in Figure 1. The unweighted least-squares line through all the points except the highest temperature one corresponds to the equation $k = 10^{11.48 \pm 0.79} \exp(-25{,}800 \pm 1400/RT)$. The highest temperature point was determined with a rather primitive mechanically stirred flow system;[6] it is included to show that the temperature dependence is not distorted by stirring limitations, which become important with the fastest reactions. The reaction was also followed in toluene, dimethylformamide, and decane solutions, using a batch method with gas chromatographic analysis. There were no detectable solvent effects on the reaction rate. The rate was about twice as fast as in the gas phase, with $\log A = 12.14 \pm 0.40$ and $E_a = 26{,}600 \pm 700$ cal/mol. This result indicates that similar conclusions may be reached from gas phase or solution phase work. We had hoped that the activation energy would allow an unequivocal distinction between a concerted reaction and a rate-determining bond rupture, but this is not the case in this parent compound, for we can roughly estimate the lower limit expected for the bond-breaking mechanism. Subtracting the resonance energy of an extra allyl radical (13 kcal)[7] from the activation energy of the methylenecyclopropane rearrangement (40 kcal)[8] (which may pass through a transition state closely resembling a diradical) leaves 27 kcal as an estimate of the bond strength. This is close to the experimental value of the activation energy and is consistent with it if this transition state also closely resembles the diradical. It should be noted that other estimates of this bond strength give rather different values; we choose this one only to suggest that we cannot unequivocally reject the diradical mechanism. A concerted reaction is also consistent with this activation energy if the bond strength was underestimated. The mechanism involving the diradical **4** is illustrated in Scheme I. In this paper we use the numerals **1**, **2**, **3**, and **4** for the unmethylated series, A–F for the monomethyl compounds, and Roman numerals for the dimethyl series. This representation of the diradical as two independent allylic radicals avoids problems of cross-conjugation and bears analogy to the "perpendicular" structure for trimethylenemethane first suggested by Gajewski.[9] It is interesting that Gajewski's discussion of the methylenecyclopropane energy surface indicates that the estimated heat of formation of the orthogonal trimethylenemethane diradical is only 27 kcal/mol above that of methylenecyclopropane.[10] This estimate, reduced by a reasonable resonance energy for the extra vinyl group, is reconcilable only with difficulty with the observed 27 kcal activation energy for the rearrangement of **1**.

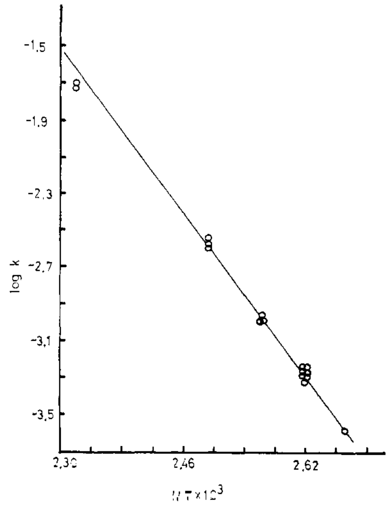
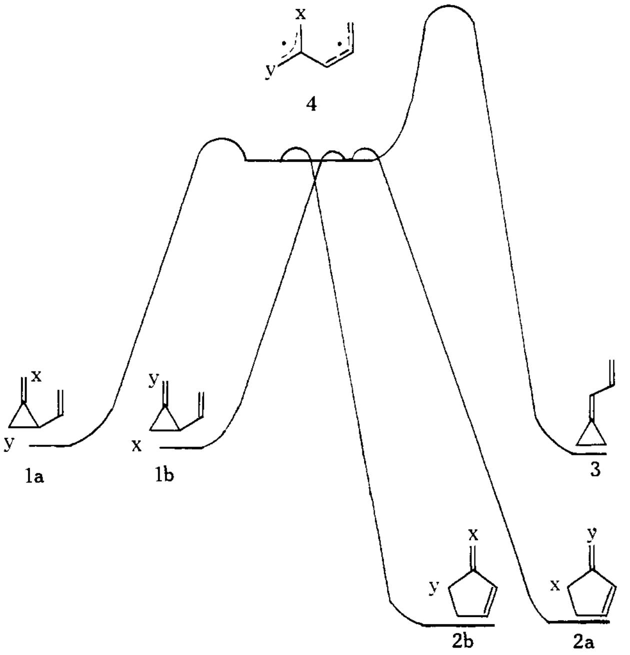


Figure 1. Arrhenius plot of the rearrangement of vinylmethylenecyclopropane.

Scheme I



J. Amer. Chem. Soc., **94**, 2116 (1972); (c) W. E. Billups, T. C. Shields, W. Y. Chow, and N. C. Deno, *J. Org. Chem.*, 37, 3676 (1972). See also J. C. Gilbert, J. R. Butler, M. Jones, Jr., and M. E. Hendrick, *Tetrahedron Lett.*, 845 (1970); W. R. Roth and Th. Schmidt, *ibid.*, 3639 (1971); M. F. Semmelhack and R. J. DeFranco, *J. Amer. Chem. Soc.*, **94**, 2116 (1972).

(5) The system is essentially the same as that described by E. S. Lewis, J. T. Hill, and E. R. Newman, *J. Amer. Chem. Soc.*, **90**, 662 (1968).

(6) We thank Mr. Robert R. Holloway for this result. Details may be found in his M.A. Thesis, Rice University, 1972.

(7) K. W. Egger, A. S. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **85**, 3346 (1963).

(8) J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 2720 (1963).

(9) J. J. Gajewski, *J. Amer. Chem. Soc.*, **90**, 7178 (1968).

(10) J. J. Gajewski, *J. Amer. Chem. Soc.*, **93**, 4450 (1971).

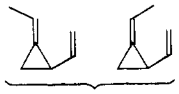
Scheme I also includes the ambiguity about the nature of the product which can be eliminated by some kind of a labeling experiment, *i.e.*, is the product from **1a**, **2a**, or **2b**?

We cannot so far distinguish between **1a** and **1b** nor between **2a** and **2b**, but all the compounds **1**, **2**, and **3** are alternative ring closure products of **4** and reactions analogous to these are all known. The observation by Gilbert[11] of the conversion **1a** → **1b** as revealed by deuterium labeling at a rate several times faster than the **1** → **2** reaction is consistent with the mechanism of this scheme and with the necessary requirement that the **4** → **1** reaction cannot have very much activation energy. We include the alternative ring closure product **3**, although it is unknown, because the analogous 2,2-dimethylallylidenecyclopropane does rearrange[3] to similar products[12] but with substantially higher activation energy (34 kcal).

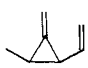
We do not believe that **3** can be a major fate of the hypothetical intermediate **4**, both because a higher activation energy is required as shown in the scheme and because it would have accumulated significantly in the conversion **1** → **2**; in fact, no significant third substance was seen in the gas chromatography of partially reacted systems. We consider it unlikely that **3** would have been overlooked, although if it had the same retention time as **2** on all columns it would have influenced neither the chromatograms nor the kinetics. Only very minor amounts of **3** would fail to show in the nmr spectra of **2**.

The distinction between the courses **1a** → **2a** *vs.* **1a** → **2b** and the detection of the reaction **1a** → **1b** require the use of some kind of label. Efforts toward the use of a ^{14}C label at the 3 position failed for lack of a degradation to find the label. We therefore adopted the use of a methyl group label as described below.

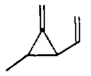
Vinylethylidenecyclopropane has been rearranged and the products have been identified.[4a] We shall consider Scheme I, with $x = CHCH_3$ and $y = CH_2$, to describe the reaction course. The representations used are A–F. All the substances A–F were isolated.



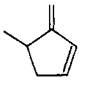
B, D



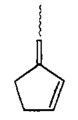
C



E



F



A

The synthetic method[4a,c] yielded a mixture of B and D. This mixture was separated by preparative gas chromatography; the individual isomers exhibited almost identical proton and ^{13}C nmr spectra. Product and rate studies were carried out on the pure isomers.

Both isomers rearrange in propylene carbonate solution following a first-order rate law. One isomer rearranged more rapidly and gave a mixture of 95% F and 5% A.[13] It is hereafter called B, and has unknown stereochemistry. The other less reactive isomer is called D; it gave 70% A and 30% F. To a good approximation both B and D were lost by a kinetically first-order process, and the rate constants were for B, $k = 10^{11.13} \exp(-23{,}700/RT)$, and for D, $k = 10^{11.73} \exp(-25{,}600/RT)$. In the case of isomer B the gas chromatogram clearly showed two minor peaks at intermediate stages of decomposition, which were identified as C and E. Both C and E were absent after all the starting B had been consumed and only A and F remained. Both C and E were identified (by retention time only) as very minor transients produced from D.

The qualitative results are fitted by the general Scheme II, in which B, C, D, and E are mutually interconvertible, but A and F are formed irreversibly. The nature of these interconversions was greatly simplified by a study of the kinetics of the intermediates C and E. These highly reactive substances, obtained by preparative gas chromatography, gave a complex mixture, striking principally in that compound F was formed extensively and compound A to a virtually undetectable extent, in times which destroyed most of C or E. Furthermore, the compound D was not observed to an important extent in the rearrangement of B, even though its low rate of rearrangement would have made it readily isolable. The scheme was therefore elaborated to that shown in Scheme III, and the rate constants which reasonably fit the data are shown in Table I, in which the rate constant k_{ij} means the rate constant for the conversion of i to j.

Scheme II

$$A \longleftarrow (B,C,D,E) \longrightarrow F$$

Scheme III

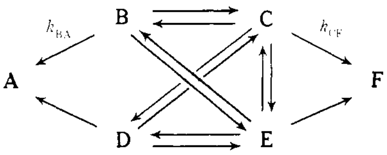


Table I. Values Chosen for k_{ij} (sec^{-1}) in Scheme III at 80.5° [a]

	i					
j	A	B	C	D	E	F
A		1.8×10^{-5}		2.7×10^{-5}	0	0
B	0		1.0×10^{-3}	0	7.0×10^{-4}	0
C	0	1.5×10^{-4}		8.0×10^{-8}	4.8×10^{-4}	0
D	0	0	1.6×10^{-4}		5.0×10^{-5}	0
E	0	3.0×10^{-4}	1.4×10^{-3}	7.3×10^{-6}		0
F	0	0	8.0×10^{-4}	0	2.8×10^{-3}	

[a] The experiments used for the basis of this table were done at temperatures of 80.5 ± 0.5°. High precision is not claimed and no effort was made to fit the rate constants to better than 10 or 20%.

The zero entries in the table have three bases. First k_{Aj} and k_{Fj} are zero because all the reactions leading

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[11] J. C. Gilbert and D. P. Highley, *Tetrahedron Lett.*, 2075 (1973). We thank Professor Gilbert for prior and subsequent communications regarding this work. This interconversion was also suggested but not demonstrated by the work of H. D. Roth, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1971, No. PET-002.

[12] A. S. Kende and E. E. Riecke, *J. Amer. Chem. Soc.*, **94**, 1397 (1972). Our preliminary gas phase measurements on a stereoisomeric mixture gave a value of 34.5 kcal, confirming the solution value above: K. H. Leavell, Ph.D. Thesis, ref 1.

[13] On all columns A was unbroadened and symmetric and the nmr did not reveal any features suggesting a mixture of stereoisomers. However, the yield from B (which is the more difficultly isolable isomer) is so small that it is not certain that the A derived from B and from D are identical, although the retention times were the same on all columns.

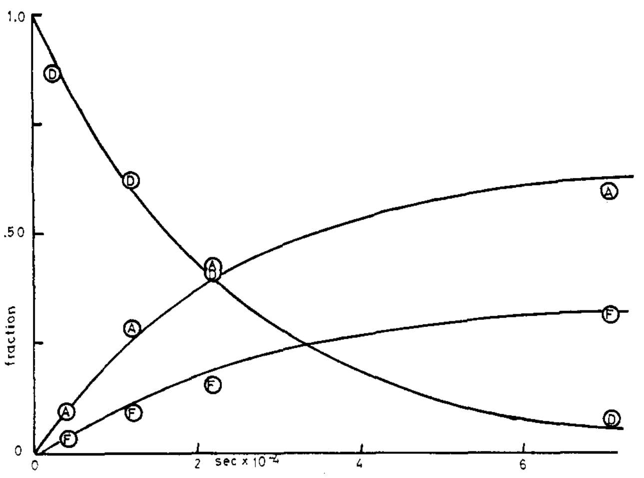

Figure 2. Rearrangement of D at 80.5°. The encircled letters in this plot of mole fraction *vs.* time are experimental points for the indicated substance, the continuous curves are those calculated from the rate constants of Table I. Compounds not shown were undetected, and the calculated concentrations were always less than 1% in the region shown. Note large differences in time scale. The plots of mole fraction of volatile materials from dilute solution in an undetected solvent are equivalent to concentrations.

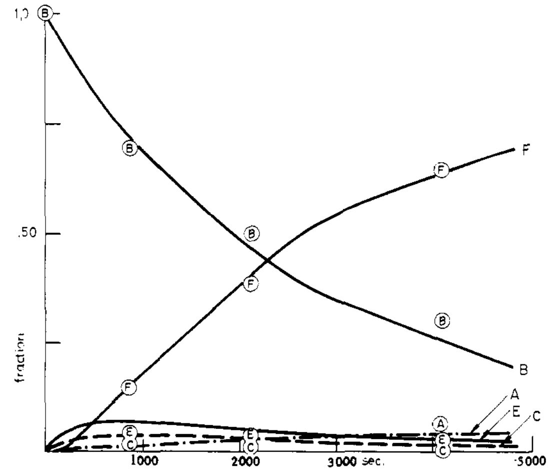

Figure 3. Rearrangement of B at 80.5°. See caption for Figure 2 for explanations. The curves at the bottom are further distinguished in that the curves for E and C go through maxima, whereas those for A and D increase monotonically. D is not shown, at 5000 sec, the calculated value is 2.8%, and observed values agree adequately with the calculations.

to A and F are apparently irreversible because of the rather large release of strain going from the cyclopropanes to the cyclopentenes. Second, k_{CA} and k_{EA} are zero because in the time given A was not formed from these substances. (B and D are formed from E and C, but the time allowed is such that B and D are virtually stable products, so that the A from them is negligible.) Third, k_{BF} and k_{DF} are written as zero because analogous 3,3 rearrangements are absent for E and C; it was of interest to see if the results could be explained without any 3,3 shifts. The very minor accumulation of D in the reaction of B could all be accounted for by the known reactions of C and E; hence k_{BD} must be smaller than any rate constants in the table; we assign zero to both it and its reverse, k_{DB}.

There were four sets of experiments used to establish the rate constants, three started with pure B, D, and E, the fourth used a mixture of 96% C with 4% E. In each experiment, samples were taken at various times and analyzed gas chromatographically for the six substances, all of which were separable on the propylene carbonate stationary phase column used. (Propylene carbonate, even at 40°, is significantly volatile so that columns do not have a long life expectancy. When *ca.* 1-μl samples of propylene carbonate solutions were injected frequently, no decay in column performance was found, and this was the reason for using this rather peculiar solvent.) Some further experiments at other temperatures, starting with B and D, were done, leading to the previously mentioned temperature dependencies, but are not further reported. One conclusion from these studies was that the amounts of C and E from the thermolysis of B increased with temperature, suggesting that the C → F and E → F processes have lower activation energies than the B → C and B → E processes.

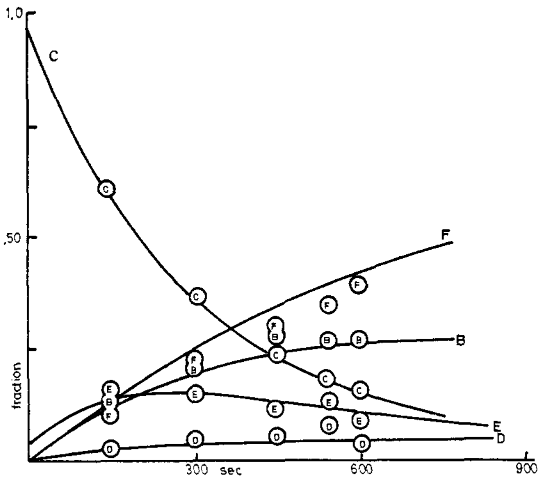

Figure 4. Rearrangement of mixture of 96% C and 4% E at 80.5°. See Figure 2 for explanation of symbols.

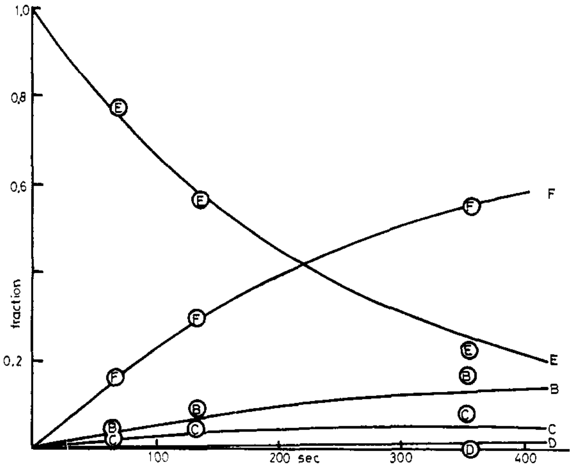

Figure 5. Rearrangement of E at 80.5°. See Figure 2 for explanation of symbols.

The data so collected allowed an initial guess of the rate constants in Scheme III, and these guesses were used as the basis of a refinement. First, the time dependence of all six substances was calculated from each of the four initial conditions, using a difference equation approach on the computer to integrate the differential equations. After a set of concentrations was calculated, it was then compared with the experimental one and new rate constants were estimated to improve the fit.

Of the 14 rate constants, only 12 are independent since there are two closed loops, and thus a restriction that the equilibrium constants (expressed as rate constant ratios) should be path independent.

Repeated attempts to fit the data showed which results were the most sensitive to which constants, and some could be established quite accurately, others less so. No attempt was made to obtain the best fit using the computer, partly because it constituted a formidable programming problem, and partly because a much better fit could not be obtained because of roughness in the data. The quality of the fit obtained after about a dozen or so adjustments is illustrated in Figures 2–5. The roughness alluded to is shown for example in the curves for E and D in Figure 4 with random deviations as big as 20% in E and 50% in D. The worst systematic deviations are the transient concentrations of C and E shown in Figure 3. The calculated curve is about twice the experimental values for both C and E. For example at about 900 sec, C_{obsd} is 0.019, C_{calcd} is 0.042. However, these concentrations have quite large errors, since they were determined from gc peaks near the lower limit of detection where some loss of very small peaks is characteristic of digital integrators. Other examples suggestive of the same error are that some substances gave no integrated peak even though the calculated amount is as much as 1–2%. The purpose of this computational exercise leading to the entries in Table I is not to establish these 14 rate constants unequivocally, but to demonstrate that Scheme III will fit the data. Inspection of Figures 2–5 supports this conclusion. It would be hard to fit the data with fewer rate constants without violating microscopic reversibility, but we cannot eliminate the possibility of the 3,3 rearrangements B → F and D → F direct processes, since the addition of further terms cannot but help the fit. Specifically, $k_{\text{BF}} > 0$ would reduce the steady-state concentrations of C and E and give better agreement. However, this disagreement, as described above, may not be significant; thus we cannot show that this extra adjustment would give a real improvement.

Within the above uncertainties, some further conclusions can be drawn from the rate constants. We can calculate with reasonable confidence the equilibrium constant $\text{C/E} = k_{\text{EC}}/k_{\text{CE}} = 0.34$, which is consistent with the nmr based structural assignment C = *cis* and E = *trans*. An equilibrium constant B/D was also calculated as $(k_{\text{DE}}k_{\text{EB}}/k_{\text{ED}}k_{\text{BE}}) = 0.3$, but because it is derived less directly, stereochemical conclusions are unreliable. The equilibrium constant C/B is 0.15, corresponding to a free energy difference of 1.3 kcal, depending on the position of the methyl group. The effect of the position of two methyl groups on the energies of 1-isopropylidene-2-vinylcyclopropane and 1-methylene-2-vinyl-3,3-dimethylcyclopropane has been estimated as $\Delta F = 3.7$ kcal.[12] Turner[14] has compared 2-methyl-1-methylenecyclopropane with ethylidenecyclopropane and finds the latter has the lower enthalpy by 3.3. kcal, but the determination has many uncertainties. Chesick[8] in the gas phase finds an enthalpy difference of only 0.5 kcal for the same pair, and the equilibrium constant extrapolated to 80° is 0.37, corresponding to our value of 0.15 for the vinyl substituted case. The results are reasonably concordant.

This study then shows the following.

(1) No [3,3]-sigmatropic shift (Cope rearrangement)[3] is required, instead all products can be explained by competing methylenecyclopropane and vinylcyclopropane rearrangements (both [1,3] shifts) and the familiar cis–trans isomerization of cyclopropanes, $\text{C} \rightleftarrows \text{E}$.

(2) The reactions of C and E must have activation energies below 23 kcal/mol, since they are substantially faster than the overall reaction of B with that activation energy.

(3) The partitioning between B and D in the reaction of E is $7 \times 10^{-4}/5 \times 10^{-5} = 14$, that in the reaction of C is $1 \times 10^{-3}/1.6 \times 10^{-4} = 6$. The difference may be significant. Similarly the partitioning between C and E in the reaction of B is $1.5 \times 10^{-4}/3 \times 10^{-4} = 0.5$, that in the reaction of D is $8 \times 10^{-6}/7.3 \times 10^{-6} = 1.1$.

We may now look at the consequences of the single diradical intermediate: (1) both the products of 3,3 and 1,3 rearrangements may be expected; (2) the bond energy is a lower limit for the activation energy; (3) the partition of a diradical among its closure products should be independent of its source.

We therefore conclude, because these consequences are not observed, that the mechanism must involve either 14 concerted reactions involving nine transition states, or a rather large number of difficultly interconvertible diradicals. The perpendicular diradical, **4** with the methyl substituent, apparently has only two stereoisomers distinguishable in these experiments (both are chiral). The only basis for the existence of more than these two diradicals would be a restricted rotation about a single bond. We therefore favor concerted mechanisms for the processes, because of the clear absence of two Cope-type closures and the fact that the other two are not needed: the low activation energies and the various unequal partitions among the products. Nevertheless, multiple diradicals (differing in rotation about single bonds) can accommodate these kinetic results, and the bond energy arguments are so rough that the low activation energies do not rigorously exclude diradicals either. The mechanism is better described than the above uncertainty suggests, for the transition states, whether or not intermediates are present, all resemble the possibly hypothetical diradicals, and the geometries, energies, and fates of these transition states are quite clear, only the number of transition states and the question of whether or not the diradicals represent shallow minima are uncertain.

The absence of [3,3] shifts is in conflict with the work of Kende and Riecke[12] who claimed that their compound V (3,3-dimethyl-2-vinyl-1-methylenecyclopropane) rearranges only *via* the methylenecyclopropane rearrangement to their compound VI (1-isopropylidene-2-vinylcyclopropane) which in turn gave concurrent vinylcyclopropane rearrangement product 3-isopropylidenecyclopentene, their II, and [3,3] rearrangement product 4,4-dimethyl-3-methylenecyclopentene, their III, as shown in their Figure 1 and Scheme IV. From the observation that III is not detected in the lower temperature V → VI conversion they deduce reasonably that II and III are both formed from VI. Reconcilia-

Scheme IV

$$\text{V} \longrightarrow \text{VI} \longrightarrow \text{II} + \text{III}$$

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(14) R. B. Turner, P. Goebel, B. S. Mallon, W. v. E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

Scheme V

$$[\mathrm{V} \rightleftarrows \mathrm{VI}] \longrightarrow \mathrm{II} + \mathrm{III}$$

tion of the two results must account for the undetectable formation of III from V (*i.e.*, <1%), the large yield of III from VI (33%), and the small equilibrium or steady-state concentration of V (0.8%) in thermolyzing VI. If our Scheme III were applied, the rate constant for V → III would be $\leq 7 \times 10^{-6}$ sec^{-1} at 80°, and $4.5 \times 10^{-5}/(3 \times 0.008) = 1.9 \times 10^{-3}$ sec at 98.6°, a totally unreasonable temperature dependence. We must conclude that the absence of 3,3 rearrangements in our system is a consequence of a special influence of the one methyl group. It is unfortunate that the generalization of one system to another is so fallible. It is possible that further studies will clarify these rather large substituent effects.

The stereochemical assignment of B and D remains unsolved. The most striking feature is the difference in the rates of methylenecyclopropane rearrangements ($k_{BC} + k'_{BE} = 4.5 \times 10^{-4}$, $k_{DC} + k_{DE} = 1.5 \times 10^{-5}$), accompanied by a smaller difference in the opposite direction for the vinylcyclopropane rearrangement ($k_{BA} = 1.8 \times 10^{-5}$, $k_{DA} = 2.7 \times 10^{-5}$). We have not been able to make a structural assignment from these observations. The other large rate difference, $k_{CF} = 8.0 \times 10^{-4}$, $k_{EF} = 2.8 \times 10^{-3}$, appears reasonable from the construction of models of the transition states; steric interaction of the *cis*-methyl and vinyl groups is significant.

There might be some value in further studies on optically active materials. However, this system is less suited to such a study than is that so clearly already worked out by Doering and Roth,[15] and the main value would be that the substituent effects are poorly understood.

Experimental Section

All starting materials were prepared as described previously.[3,4a] Vinylmethylenecyclopropane was isolated in sufficient purity for kinetic runs by bulb to bulb distillation. The *syn*- and *anti*-vinylethylidenecyclopropane isomers (B and D, not necessarily respectively) were separated by preparative glpc on a 0.25-in. column packed with 15% propylene carbonate on Chromosorb P.

The flow system used to make rate measurements has been previously described.[5] Prepurified nitrogen gas controlled by a needle valve is passed through a sulfuric acid pressure regulator. Fine flow rate control is obtained by the use of a second needle valve after the regulator. Flow rates are visually set by the use of a flowmeter (a water manometer containing a dye across which there is a pressure drop caused by a long capillary tube). Any moisture evolving from the flowmeter is removed by a drying tower.

This constant flow of dry nitrogen gas is then bubbled through a jacketed, thermostated vaporizer where the gas is saturated with the vapor of the compound to be studied. The vaporizer jacket temperature is held constant to within ±0.05° by a Lauda Ultra-Thermostat circulator. From a knowledge of the vapor pressure of the compound to be studied at the temperature of the vaporizer, the concentration of entering reactant in the vapor stream is known. The gas stream passes into a quartz or Pyrex glass reaction vessel which is surrounded by an insulated aluminum block. The temperature of the aluminum block is controlled to ±0.05° by use of a heating tape which is connected to a Hallikainen Instrument's Thermotrol.

The gaseous mixture passes into and out of the reaction vessel through capillary tubing whose volume is negligible compared to the volume of the reaction vessel. Perfect mixing is assumed to be attained within the reactor. The outflowing gases can be analyzed directly by analytical gas chromatography. Flow rates are measured with a soap bubble flowmeter and are connected to the reactor temperature by the ideal gas law.

Table II. Time and Temperature Dependence of Concentrations of Intermediates E and C, Compared with that of the Reagent, B

Temp, °C	Time, sec	E/B	C/B
80.6	910	0.045	0.022
80.6	2100	0.052	0.035
80.6	4080	0.052	0.018
88.9	600	0.059	0.029
88.9	1260	0.057	0.025
88.9	2880	0.052	0.021
88.9	6000	*a*	*a*
99.1	212	0.047	0.027
99.1	591	0.056	0.028
99.1	685	0.064	0.028
99.1	1500	0.054	0.03
109.5	120	0.076	0.04
109.5	240	0.081	0.042
109.5	420	0.084	0.042
109.5	600	0.062	0.021
126.7	59	0.089	0.053
126.7	98	0.08	0.048
126.7	98	0.07	0.031

[a] At this time neither B, C, nor E was detectable in significant amount.

First-order rate constants are calculated from the following equation, where U is the flow rate (ml/sec), V is the volume of the reactor, and [B] and [A] are the steady-state concentrations of product and starting material flowing from the reactor.

The solution kinetics on vinylmethylenecyclopropane were run by adding the hydrocarbon to the appropriate solvent in a 25-ml volumetric flask and filling to the mark. About 0.5-ml portions of this solution were added to 1-ml Neutraglas ampoules from the Kimble Glass Co. These ampoules were cooled to liquid nitrogen temperature and sealed under vacuum. Several of these were then submerged simultaneously into a large constant-temperature (±0.05°) oil bath. At known times samples were removed, quenched rapidly in ice-water, and analyzed by gas chromatography. The rates on B, C, D, and E were run similarly except that the total volumes used were much smaller. The sealed tubes were melting point capillaries and contained only about 2 μl of solution, and a substantial fraction of this was injected into the gas chromatograph. First-order rate constants, where applicable, were calculated conventionally by comparing the integrated areas of the reagent with that of all products. Integrations were done with an electronic digital integrator, and results were quantitatively reproducible and in agreement with other area measurements except for the smallest peaks, where all methods had large errors. In addition to the results shown in Figures 2–5, data on the accumulation of C and E from B at several other temperatures are presented in Table II, which shows that a steady-state ratio of C/B and E/B is rapidly attained.

Gas chromatographic analyses were performed on a Varian Aerograph 500D chromatograph equipped with a hydrogen flame detector. Peak area ratios were assumed to be proportional to mole ratios, since all compounds compared are isomeric. A 10 ft × $^1/_8$ in. column packed with 15% FFAP on Chromosorb P was used for the vinylmethylenecyclopropane–methylenecyclopentene analysis. The vinylethylidenecyclopropane system was followed by using a 12 ft × $^1/_8$ in. column packed with 15% propylene carbonate on Chromosorb P. The column temperature was kept below 40°, allowing all substances to pass through the column without detectable rearrangement. Injection temperatures low enough to prevent rearrangement were attainable for small samples. The sequence of elution of these isomers on this column was E, C, D, B, F and A, and the spacing made the separation of B from F the most difficult of these. Identification of A and F and of the B–D mixture had already been done by primarily nmr methods.[4c] The proton and ^{13}C spectra of the separated B and D did not differ enough to allow structural assignment, although the more inaccessible B was not thoroughly studied. Decoupling and Overhauser enhancement measurements of potential value in distinguishing have also not been done, because of both poor resolution and insufficient compound.

Compounds C and E were isolated by gas chromatography on a propylene carbonate column at room temperature of a sample of mixed B and D heated in sealed ampoules at as high a temperature as practical for a time corresponding to about 15% reaction of B, because the yields of C and E increase with temperature; most work was done at about 130°. Some of these small sealed samples ex-

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(15) W. v. E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

ploded in the oil bath used, and at higher temperatures this was even more of a problem. Since the reaction is highly exothermic and the compounds probably boil at near 100°, these small explosions probably resulted merely from the vapor pressures of samples rather hotter than the bath. Explosions of the solvent diluted samples used in kinetic work were not observed.

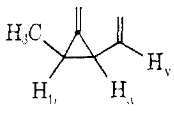
The proton spectra of C and E used for structural assignment were taken at 60 MHz in carbon disulfide at temperatures low enough to prevent rearrangement. The spectra were very noisy and did not show all details, but the following features allowed an assignment.

(1) E and C both showed olefinic absorption essentially identical with that of the parent compound[8] within the available precision. This allows the methyl substituent to be only at the 3 position.

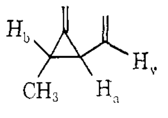
(2) In the saturated region E showed a somewhat broad single peak at δ 1.2, and a weaker doublet ($J \sim 9$ Hz, δ 1.64).

(3) In the saturated region C showed a doublet ($J \sim 6$ Hz, δ 1.07) with the low-field component 1.8 times as strong as the high field one. The doubly allylic proton must have been broader or more split than in E, or it would have been visible over the noise level.

We assign structures and peaks as follows using the notation illustrated.



C



E

In C the methyl group (δ 1.07) is coupled to H_b, and using the AB_3 models from Wiberg and Nist,[16] we deduce that H_b should center at roughly δ 1.50, but the coupling with H_a and with the methyl protons keeps it invisible. Similarly H_a is invisible because of two large couplings with H_b and H_v.

In E, the methyl group signal is largely in the single peak at δ 1.2, implying that for H_b δ is rather close to this value. H_b is itself not visible, presumably it is too highly split. Again using the Wiberg and Nist models we conclude that for H_b $\delta \leq 1.38$. H_a is visible and lies at δ 1.64 showing only one large coupling, presumably with H_v. The coupling to H_b is apparently much smaller, as is usually the case in *trans*-cyclopropyl protons.[17]

The stereochemical assignment is based on several factors. First, E, relative to the parent compound, is missing a large coupling in H_a, hence the H_b is trans to H_a. Second, the invisible H_b absorbs at smaller δ in E than in C, and in the parent the small δ signal is associated with the proton cis to the vinyl group. Third, the methyl protons in C are more shielded than those in E, consistent with a position cis to the vinyl group.

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(16) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, New York, N. Y., 1962, p 303.

(17) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, 1969, p 286.

Photobenzidine Rearrangements. III. The Photochemistry of 1,4-Diaryl-1,4-dimethyl-2-tetrazenes[1,2]

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Abstract: The photodecomposition of a series of 1,4-diaryl-1,4-dimethyl-2-tetrazenes in solution has been shown to produce the corresponding *N,N'*-dimethylhydrazoaryls as the major photoproducts. The quantum yields for photodecomposition with various aryl substituents were found to be (methanol solution): *p*-CO_2Et, 0.41; *p*-Cl, 0.21; *p*-H, 0.21; *p*-CH_3, 0.16; *p*-OEt, 0.08. A similar trend was found for quantum yields of decomposition in cyclohexane. The tetrazenes have been found to fluoresce at 77°K in ethanol and their fluorescence quantum yields were measured: *p*-CO_2Et, 0.6; *p*-Cl, 0.3; *p*-H, 0.1; *p*-CH_3, 0.1; *p*-OEt, 0.04. Sensitization experiments with acetone and phenanthrene and quenching experiments with oxygen and piperylene indicate a singlet state reaction. It is concluded that the variations in quantum yields of decomposition at 25° and of fluorescence at low temperature reflect the effect that substituents have on intersystem crossing to a nonreactive triplet state.

In an earlier publication we illustrated the connection between the photochemistry of 1,4-dimethyl-1,4-diphenyl-2-tetrazene (**1a**) and *N,N'*-dimethylhydrazobenzene (**2a**).[4] It was shown that **2a** rearranged to the *p*-semidine (**3**) when irradiated in hexane solution, and that, when similarly irradiated, **1a** gave **2a** in good yield accompanied by *N*-methylaniline and some of **3**. Subsequently, it was shown that the photorearrangement of some other *N,N'*-dimethylhydrazobenzenes occurred quite easily.[2] We have turned our attention now to analogous 1,4-dimethyl-1,4-diaryl-2-tetrazenes in order to learn more about their photodecomposition.

Few reports on the photochemistry of 2-tetrazenes are to be found in the literature. A number of 1,4-dialkyl-1,4-diphenyl-2-tetrazenes (dimethyl, diethyl, dipropyl, dibutyl) were reported by Child and coworkers to undergo photodecomposition,[5] among which **1a** gave **2a** and *N*-methylaniline (**4a**). Imoto's group has found that **1a** is moderately active in photoinitiating the polymerization of styrene and other monomers.[6] The formation of *o*- and *p*-chloroacetanilide from photolyzing 1,4-diacetyl-1,4-diphenyl-2-tetrazene in solutions of chlorine atom donors has been interpreted as involving the photodecomposition of the tetrazene.[7] In none of these reports is detailed information given on the way in which light initiates the decomposition of tetrazenes, except for the deduction[6,7]

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(1) Supported by Grant No. D-028 from the Robert A. Welch Foundation.

(2) Part II: H. J. Shine and J. D. Cheng, *J. Org. Chem.*, **36**, 2787 (1971).

(3) Postdoctoral Fellow.

(4) J. F. Sullivan, K. Hailey, and H. J. Shine, *Tetrahedron Lett.*, 2007 (1970).

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