Synthesis of an Optically Active Cyclopropene and Kinetics of Its Thermal Racemization in the Gas Phase. Evidence for the Intermediacy of a Vinylcarbene

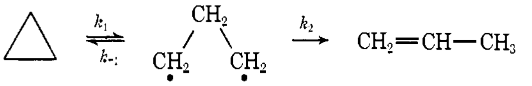
Eunice J. York, Wolfgang Dittmar, J. Ronald Stevenson, and Robert G. Bergman*[1]

Contribution No. 4690 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

Received April 12, 1973

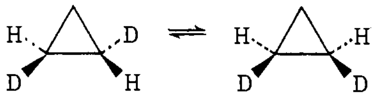
Abstract: Optically active 1,3-diethylcyclopropene has been prepared; on pyrolysis in the gas phase at three temperatures it undergoes racemization ($E_a = 32.6$ kcal/mol, $\log A = 11.8$) considerably faster than it is converted to a mixture of substituted diene and acetylene products. The cyclopropene must therefore undergo ring opening, bond rotation, and recyclization at a surprisingly rapid rate, considering that the closed ring has 54 kcal/mol of strain energy. Thermochemical analysis of the reaction suggests that ring cleavage and rotation occur simultaneously, leading directly to a vinylcarbene intermediate which may be similar or identical with the type of intermediate generated in the thermal decomposition of vinyl diazo compounds. The relationship of these observations to the problem of barriers to ring closure in biradicals, and to substituent effects in small ring thermal decompositions, is discussed.

Studies of the thermal chemistry of cyclopropane and its derivatives have played an important role in the development of our understanding of the mechanisms by which carbon–carbon bonds may be broken and re-formed.[2] Discovery of its clean, unimolecular rearrangement to propylene led to the postulate that carbon–carbon bond cleavage in cyclopropane led initially to a "trimethylene biradical" (**2**), which could then suffer hydrogen shift to give the olefinic product.[3a] Evidence for the existence of such an intermediate was obtained by Rabinovitch, Schlag, and Wiberg, who found that cis–trans or "geometrical" isomerization in 1,2-dideuteriocyclopropene (**4**) was a process competitive with rearrangement to propylene-d_2 ("structural" isomerization); their results also indicated that ring closure and hydrogen shift in the postulated intermediate were characterized by rate constants (k_{-1} and k_2) of similar magnitude.[3b] In a later study aimed at detecting electrocyclic processes in cyclopropane thermolyses, our group[3c,e] and Berson's[3d] found that ring closure and bond rotation occurred at competitive rates in substituted analogs of **2**.



1 2 3

Thermochemical analysis of the cyclopropane system by Benson and coworkers has led to the suggestion that there is a significant barrier to ring closure in **2** of the order of 9–10 kcal/mol.[4] This barrier has been accounted for by assuming that the transition state for ring closure incorporates some of the strain energy associated with the fully formed three-membered ring.[4c] Recent theoretical work, however, has suggested that the ring-closure barrier is much lower and may, in fact, be nonexistent.[5] The question as to whether or not this barrier has a significant magnitude now stands as one of the central problems in the chemistry of 1,3 and other biradicals.[6a]



4T **4C**

We felt that an examination of the thermal chemistry of cyclopropene (**5**), an unsaturated relative of cyclopropane, might shed some light on this problem, since cyclopropene has nearly twice the strain energy of cyclopropane.[6b] If incipient ring strain is in fact the source of small-ring biradical ring closure barriers,[4c] one might expect any barrier in **6**, the biradical derived from **5**, to be much higher than that postulated for **2**. Such a study might also be important for other reasons—for example, presumed intermediate **6** is a "vinyl, alkyl" biradical, which might show other chemical behavior quite different from that of **2**; in addition, **6** is almost unique in that it is structurally very

---

[1] (a) Alfred P. Sloan Foundation Fellow, 1971–1972; (b) Camille and Henry Drefus Teacher-Scholar, 1970–1975.

[2] For leading references, see (a) H. M. Frey, *Advan. Phys. Org. Chem.*, 4, 147 (1966); (b) R. G. Bergman in "Free Radicals," J. Kochi, Ed., Vol. I, Wiley, New York, N. Y., 1973; for a preliminary report of this work, see (c) E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *J. Amer. Chem. Soc.*, 94, 2882 (1972).

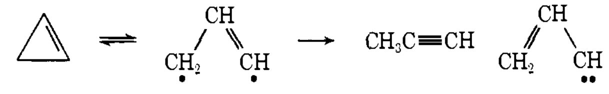
[3] (a) T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **56**, 399 (1934); (b) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, 28, 504 (1958); (c) W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, 90, 7344 (1968); (d) J. A. Berson and J. B. Balquist, *ibid.*, 90, 7343 (1968); (e) R. G. Bergman and W. L. Carter, *ibid.*, **91**, 7411 (1969).

[4] (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968); (b) *Int. J. Chem. Kinet.*, 2, 423 (1970); (c) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, 38, 18 (1963); (d) S. W. Benson, *ibid.*, 34, 521 (1961).

[5] (a) R. Hoffmann, *J. Amer. Chem. Soc.*, 90, 1475 (1968); (b) E. F. Hayes and A. K. Q. Siu, *ibid.*, 93, 2090 (1971); (c) R. J. Buenker and S. D. Peyerimhoff, *J. Phys. Chem.*, 73, 1299 (1969); (d) A. K. Q. Siu, W. M. St. John, and E. F. Hayes, *J. Amer. Chem. Soc.*, 92, 7249 (1970); (e) P. J. Hay, W. J. Hunt, and W. A. Goddard, *ibid.*, 94, 638 (1972); (f) J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, 94, 279 (1972).

[6] (a) L. M. Stephenson, T. A. Gibson, and J. I. Brauman, *J. Amer. Chem. Soc.*, in press; (b) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, 90, 4315 (1968).

closely related to a "carbene"-type intermediate (8).[7]



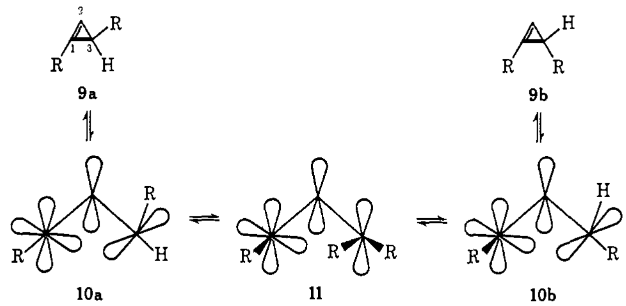
5 6 7 8

We were therefore interested in determining whether the intermediate generated in the pyrolysis of **5** was related (or identical) to that generated in the decomposition of vinyldiazomethane.[7]

Little was known about the thermal chemistry of simple cyclopropenes at the time we began this study. However, Wiberg and Bartley had observed[8] in 1959 that cyclopropene itself rearranged thermally to methylacetylene (**7**), a reaction quite analogous to the formation of propylene from cyclopropane. We therefore set out to determine whether a process which could be associated with ring opening and ring closure, perhaps *via* some type of biradical intermediate, was competitive with structural isomerization in the cyclopropene system.

Unfortunately, the presence of a double bond in the three-membered ring eliminates two of the three tetravalent centers which are present in cyclopropane, and hence the sort of cis–trans isomerization study carried out by Rabinovitch, Schlag, and Wiberg on 1,2-dideuteriocyclopropane[3b] cannot be applied to cyclopropene. However, inspection of possible modes of ring opening and rotation in appropriately substituted cyclopropenes suggests a somewhat different way of detecting these molecular motions. As an example (*vide infra*), consider the 1,3-disubstituted cyclopropene derivative (**9a**) shown in Scheme I. Ring opening with no concurrent rotation leads to intermediate **10a**, in which the new "radical" orbital at C-3 is orthogonal to the double bond π orbitals. For the purposes of discussion, let us call this the "biradical" intermediate. It seems likely that such a species will want to take advantage of the potential allylic resonance energy[9] inherent in overlap of C-3 with C-2; this can occur by rotation through 90° to give "carbene" intermediate **11**. If this entire process is reversible, **11** may return though **10a** and ring close to **9a**. However, because it now has a plane of symmetry, an equally probable motion is rotation in the opposite sense to give **10b** followed by ring closure to **9b**. Examination of structures **9a** and **9b** shows that they are chemically identical but nonsuperimposable; *i.e.*, they are enantiomers. Thus the operation of the process outlined in Scheme I, at a rate competitive with product formation, would result in racemization of an optically active 1,3-disubstituted cyclopropene derivative. This paper reports the search for and discovery of such a racemization process.

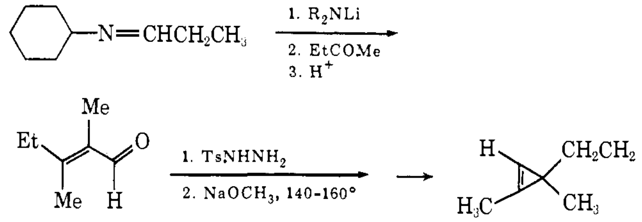
Scheme I

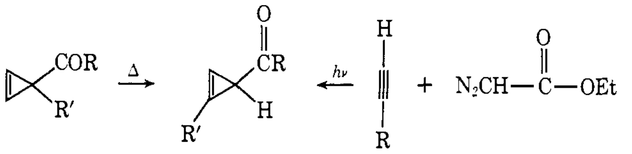


R = CH₂CH₃

Synthesis. At the beginning of this study, no simple cyclopropene derivatives had been prepared in optically active form,[10] and the number of methods available for the synthesis of even racemic materials was (and still is) severely limited. We therefore investigated several possible routes; those which proved unsuccessful will be mentioned only briefly here. 3-Ethyl-1,3-dimethylcyclopropene was prepared by the sequence outlined in Scheme II,[11] but asymmetric hydroboration[12] of this olefin using a deficiency of reagent occurred quite slowly and without optical fractionation. In other routes, the addition of carbomethoxycarbene to 1-pentyne was carried out,[13] as was the more lengthy preparation of 1-methyl-3-acetylcyclopropene.[14] However, both of these methods were abandoned because the sensitivity of the cyclopropene double bond prevented successful reduction of the carbonyl group. Finally, 2-bromo-2,3-dimethylcyclopropanecarboxylic acid[15] was prepared (Scheme III), in hopes that the acid could be resolved by recrystallization of a salt formed with an optically active amine, and then converted to 1,3-dimethylcyclopropene by bromodecarboxylation. Pyrolysis of the sodium salt of the acid, however, gave only 3,4-dimethylbutenolide; no cyclopropene derivative was detected.

Scheme II





---

(7) See, for example, (a) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 99 (1963); (b) G. L. Closs, L. E. Closs, and W. A. Boll, *ibid.*, **85**, 3796 (1963); (c) H. Dürr, *Chem. Ber.*, 103, 369 (1970); (d) T. Severin, H. Krämer, and P. Adhikary, *ibid.*, **104**, 972 (1971); (e) M. E. Hendrick, W. J. Baron, and M. Jones, Jr., *J. Amer. Chem. Soc.*, **93**, 1554 (1971); (f) M. E. Hendrick, *ibid.*, **93**, 6337 (1971); (g) M. Franck-Neumann, *Tetrahedron Lett.*, 15 (1969); (h) G. Baum, R. Bernard, and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5307 (1967); (i) G. Büchi and J. D. White, *ibid.*, **86**, 2884 (1964); (j) G. Snatzke and H. Langen, *Chem. Ber.*, **102**, 1865 (1969); (k) L. Schrader, *ibid.*, **104**, 941 (1971); (l) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967).

(8) K. B. Wiberg and W. J. Bartley, *J. Amer. Chem. Soc.*, **82**, 6375 (1960).

(9) (a) D. M. Golden, *Int. J. Chem. Kinet.*, **1**, 127 (1969); (b) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2136 (1969); (c) R. J. Field and P. I. Abell, *ibid.*, **91**, 7226 (1969).

(10) For an example of a more highly substituted, optically active cyclopropene derivative, see R. Breslow and M. Douek, *J. Amer. Chem. Soc.*, **90**, 2698 (1968).

(11) G. Wittig and H. Reiff, *Angew. Chem., Int. Ed. Engl.*, **7**, 7 (1968).

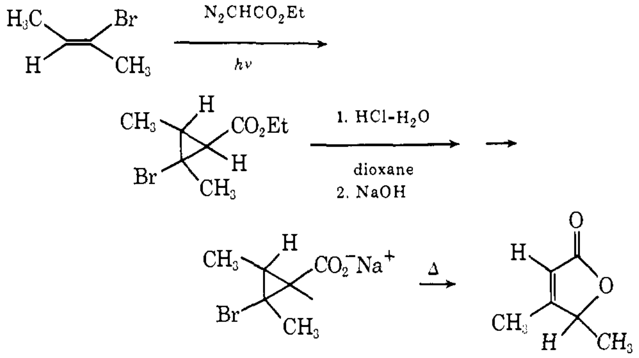
(12) (a) W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968); (b) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 1071 (1964).

(13) (a) M. Vidal, I. Massot, and P. Arnaud, *C. R. Acad. Sci. Ser. C*, **268**, 423 (1969); (b) M. Vidal, Thesis, University of Grenoble, France, 1970.

(14) H. Monti and M. Bertrand, *Tetrahedron Lett.*, 1235 (1969).

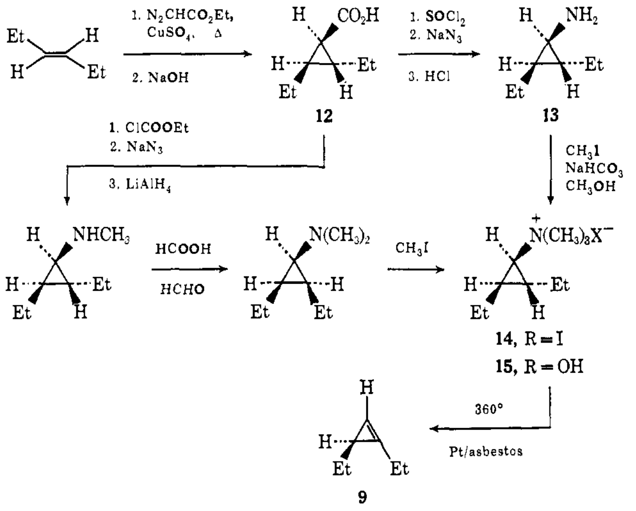
(15) (a) M. Vidal, J. Pierre, and P. Arnaud, *C. R. Acad. Sci.*, **269**, 599 (1969); (b) J. A. Carbon, W. B. Martin, and L. R. Swett, U. S. Patent 2,966,536; *Chem. Abstr.*, **56**, 1362 (1962).

Scheme III



Success was finally achieved using the classic cyclopropene synthesis from quaternary amine hydroxides employed by Schlatter in the preparation of the parent compound.[16] *cis,trans*-2,3-Diethylcyclopropanecarboxylic acid (**12**) was prepared and resolved using the method of Walbrick, Wilson, and Jones.[17] The racemic material was then converted (*via* amine **13** and its substituted analogs) to the corresponding trimethylammonium iodide **14** by the routes outlined in Scheme IV,

Scheme IV



and to the hydroxide (**15**) by exchange of the iodide with silver oxide in water. Pyrolysis of the hydroxide at 360° on a platinum/asbestos catalyst in a vessel connected to a vacuum trap[16] gave 1,3-diethylcyclopropene (**9**), along with a significant amount of recovered amine. When optically active material (of undetermined absolute configuration and optical purity) was carried through the synthetic route, acid **12**, $[\alpha]^{25}\text{D}$ −4.8°, gave diethylcyclopropene with $[\alpha]^{25}\text{D}$ +34.0°. Structural identity of optically active and racemic materials was established spectroscopically at each point along the route (see Experimental Section).

Pyrolysis of 1,3-Diethylcyclopropene. Thermolysis of racemic cyclopropene **9** gave a mixture of four products which could be separated into only three fractions by preparative vapor chromatography. Both the early and late eluting peaks proved to be pure compounds; they were assigned the 2,4-heptadiene gross structure by comparison with commercially available authentic samples.[18a] The stereochemistry of the early peak was assigned by comparing its 220-MHz nmr spectrum with that of the 2,4-hexadienes. The chemical shifts and splitting patterns of the vinyl protons were very similar to those of *trans,trans*-2,4-hexadiene and thus the same stereochemistry (**16**) was assigned to this molecule. The *trans*-methyl, *cis*-ethyl stereochemistry was assigned to the latest eluting peak (**17**) on the basis of the similarity of vinyl hydrogen chemical shifts and coupling constants with those of *cis,trans*-2,4-hexadiene, and also by comparison of the chemical shifts of the allylic methyl groups in **16**, **17**, and 2,4-hexadiene.

The middle eluting peak consisted mainly of 3-heptyne (**18**), identified by comparison of its nmr spectrum with that of an authentic sample,[18b] contaminated with about 10% of a third diene. The structure of the diene was assigned the *cis*-methyl, *trans*-ethyl stereochemistry (**19**), again on the basis of comparison of nmr chemical shifts and coupling constants with the hexadienes.

By employing a combined gc–nmr analysis, the product distribution (essentially independent of temperature) was found to be **16**, 34%; **17**, 29%; **18**, 33%; and **19**, 4%.

Pyrolysis kinetics were carried out in a static reactor constructed of lead–alkaline glass[19] (about 200 ml volume) connected to a vacuum line. The reactor was immersed in a stirred bath of high-temperature oil. Cyclopropene thermal decomposition kinetics can sometimes be complicated by surface effects,[20] but this appears to be strongly dependent on substitution. In the case of diethylcyclopropene, some care had to be exercised, but in properly conditioned reactors, the rates of decomposition could be shown to be independent of surface/volume ratio. Good first-order dependence of the rate data was also obtained, indicating that the decomposition is a true unimolecular reaction. Previous work[20a,b] indicates that the pressures used in this study were well into the high-pressure region for the decomposition. The rate constant for overall conversion of **9** to products (k_i) was measured at three temperatures over a 30-degree range; the activation parameters determined by least-squares analysis were $\log A = 10.4$, $E_a = 32.2$ kcal/mol (Table I).

In order to measure the kinetics of racemization of optically active **9**, for each point taken a sample of the cyclopropene was vaporized into the reactor, allowed to react for a specified length of time, and then distilled out and analyzed polarimetrically. It was indepen-

---

(16) M. J. Schlatter, *J. Amer. Chem. Soc.*, **63**, 1733 (1941).

(17) J. M. Walbrick, J. W. Wilson, and W. M. Jones, *J. Amer. Chem. Soc.*, 90, 2897 (1968). Drawings are not intended to reflect actual absolute configurations.

(18) (a) Aldrich Chemical Corp.; *cf.* A. L. Henne and A. Turk, *J. Amer. Chem. Soc.*, **64**, 827 (1942); (b) Farchan Chemicals; *cf.* J. H. Wotiz and F. A. Miller, *ibid.*, 71, 3441 (1949).

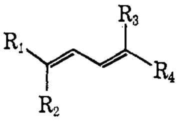
(19) Corning Potash Soda Lead No. 0120 Glass was employed (Professor W. von E. Doering, private communication).

(20) One troublesome aspect of cyclopropene kinetics, reported with earlier structural isomerization data[20a,23b] and reflected both in our product formation and racemization studies (see Table I), is that the frequency factors for pyrolysis are very often too low (*i.e.*, the entropies of activation are somewhat negative, whereas a somewhat positive $\Delta S^{\ddagger}$ is predicted using thermochemical calculations). This problem is often characteristic of gas-phase reactions which are complicated by surface effects, but (as described in the text and experimental) both our own rates and those of others[20a,b] have been shown to be essentially independent of changes in the surface : volume ratio of the reaction vessel. This is the conventional method of obtaining suggestive evidence of surface independence; however, we are investigating this problem more thoroughly by examining the decomposition kinetics of certain cyclopropenes in a "wall-less" reactor, which we have recently constructed following the design of Taylor, Hutchings, and Frech.[20c] (a) R. Srinivasan, *J. Amer. Chem. Soc.*, 91, 6250 (1969); (b) R. Srinivasan, *J. Chem. Soc. D*, 1041 (1971); (c) J. E. Taylor, D. A. Hutchings, and K. J. Frech, *J. Amer. Chem. Soc.*, 91, 2215 (1969).

Table I. Rate Constants and Arrhenius Parameters for Gas-Phase Thermal Racemization and Structural Isomerization of Optically Active 1,3-Diethylcyclopropene (**9**)

Rate constants[a,b] ($\times 10^6$), sec^{-1}	Temp, °C			Arrhenius parameters[c,d]	
	161.1	175.6	190.4	Log A	E_a
k_α	2.69	8.04	29.6	11.8	32.6
$k_i = k_P$	0.151	0.415	1.61	10.4	32.2
k_{DL}	1.27	3.81	14.0	11.5	32.7
k_{DL}/k_P	8.4	9.2	8.7		

[a] For a definition of rate constant symbols, see the text. [b] Error limits in the reported rate constants are generally ±3%. [c] Error in log A is ±1 log unit; error in E_a is ±1.5 kcal/mol. [d] $\Delta H^{\ddagger}$ (see text) calculated using the equation $\Delta H^{\ddagger} = E_a - nRT$ with $n = 1$ and $T = 448$ °K. Energy units are kcal/mol.



16, $R_1 = CH_3$; $R_2 = R_3 = H$; $R_4 = Et$

17, $R_1 = CH_3$; $R_2 = R_4 = H$; $R_3 = Et$

19, $R_1 = R_3 = H$; $R_2 = CH_3$; $R_4 = Et$

$CH_3CH_2C{\equiv}CCH_2CH_2CH_3$

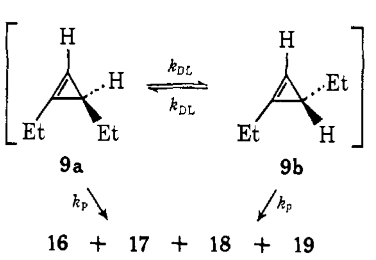
18

dently shown by preparative vpc on selected samples that the products of the reaction were completely inactive. A plot of the log of the specific rotation of the pyrolysate *vs.* time was nicely linear, indicating that overall loss of optical activity was a first-order process. The rate constant for this process was termed k_α and it was measured at the three temperatures used for the determination of k_i (Table I). The activation energy for overall loss of optical activity (32.6 kcal/mol) was identical within experimental error with that measured for k_i, but the frequency factor was somewhat higher (log A = 11.8).

Discussion

It is clear from the values of k_α and k_i (Table I) that during pyrolysis, 1,3-diethylcyclopropene (**9**) loses optical activity faster than it is converted to pyrolysis products. These phenomenological rate constants can be converted to the important unimolecular rate constants by reference to Scheme V. If we let k_{DL} be the

Scheme V

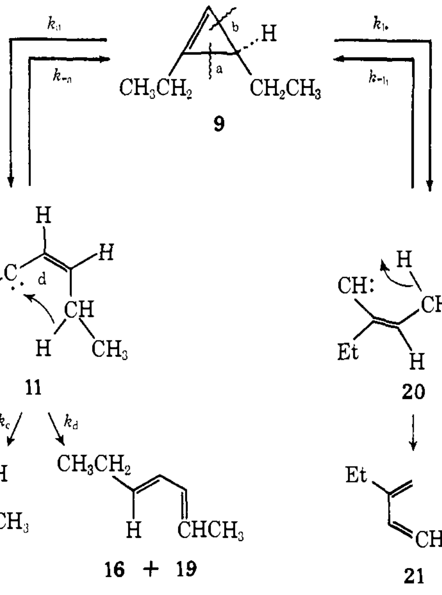


rate constant for transformation of **9a** into its enantiomer **9b**, and k_P be the rate constant for transformation of **9** into products, solution of the kinetic equations describing this system leads to $k_i = k_P$ and $k_\alpha = 2k_{DL} + k_P$. Using the measured k_α and k_i data to solve these equations shows that at all three temperatures, k_{DL} is about nine times larger than k_P; *i.e.*, nine molecules of **9** are enantiomerized for every molecule converted to products.

Assuming that racemization does not occur by unprecedented, orbital-symmetry-forbidden 1,3-hydrogen shift,[21] it must be produced by the sort of ring-opening, rotation, ring-closure process outlined in Scheme I. Thus if ring opening and rotation in **9a** generate intermediate **11**, this species can apparently rotate back into conformation **10b** (which requires a loss of at least some allylic stabilization), and can also reclose to the cyclopropene (at the cost of a significant amount of strain energy).

The actual set of ring-opened intermediates in the case of the **9** pyrolysis may be somewhat more complex than is indicated in Scheme I. At present we have no rigorous information concerning the relative amounts of cleavage of the two three-membered ring σ bonds in **9**; cleavage on either side can, of course, lead to racemization (*cf.* Scheme VI). Inspection of the products, however, suggests that only the most highly substituted bond is breaking. Once carbene **11** is formed, there are then two possible paths for its conversion into dienes **16**, **17**, and **19**. One mode (c) involves 1,2-hydrogen shift from the methylene adjacent to the carbene center;[22] the other (d) involves 1,4 shift from the methylene group on the other side of the molecule. Unfortunately, the symmetry inherent in **9** prevents us from distinguishing the relative abundances of the two pathways in the present system without isotopic labeling experiments; however, products formed in other substituted cyclopropene pyrolyses indicate that the two paths are normally competitive.[20,23] It is clear that opening the less substituted bond (to give **20**) cannot lead to 1,2-shifted product, but 1,4 shift is still possible and should lead to 4-ethyl-2,4-pentadiene (**21**). None of this material is formed; it is possible that this is due to some unforseen slowness in the rate constant for 1,4 shift in **20**, but it is probably more reasonable to interpret this observation as an indication that $k_a \gg k_b$.

Scheme VI



---

[21] For example, 1- and 3-methylcyclopropene do not interconvert on pyrolysis.[20a] That 1,3-alkyl shift is not responsible for racemization is suggested by the observation that 1,3- and 3,3-dimethylcyclopropene do not interconvert thermally.[20b]

[22] W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, Chapters 7 and 12.

[23] (a) H.-H. Stechl, *Ber.*, 97, 2681 (1964); (b) R. D. Streeper and P. D. Gardner, *Tetrahedron Lett.*, 767 (1973).

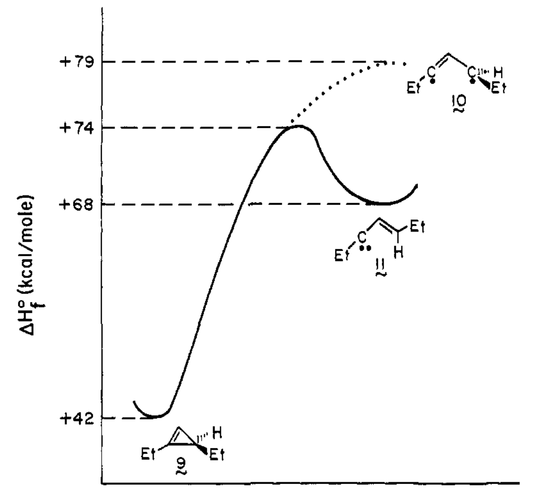
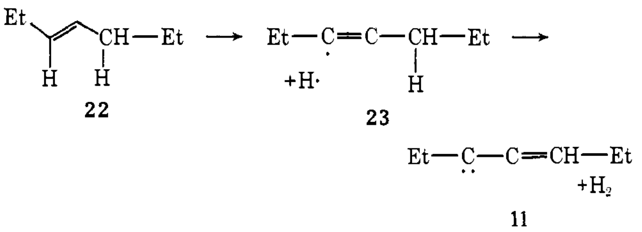


Figure 1. Possible reaction coordinate for ring opening of 1,3-diethylcyclopropene (**9**).

If we assume, as a working hypothesis, that path a (Scheme VI) is the major mode of reaction in cyclopropene **9**, we can use the techniques of thermochemical analysis to provide some interesting insights into the racemization reaction. One can reliably estimate the heat of formation of **9** to be +42 kcal/mol.[24] The heat of formation of **11**, the vinylcarbene derived from **9**, is estimated by employing the energies indicated in the thermodynamic sequence pictured in Scheme VII.[25]

Scheme VII



The heat of formation of *trans*-3-heptene (**22**) is −17.4 kcal/mol.[24] The "secondary" vinyl C–H bond energy is not known, but if alkyl stabilization effects in alkyl and vinyl radicals are similar, we can estimate the energy of the vinyl C–H bond in 3-heptene as that of ethylene (108 kcal/mol) less about 3 kcal/mol.[24] This gives a value for the heat of formation of radical **23** of −17.4 + 105 = +87.6 kcal/mol. In order to reach the carbene intermediate, we must remove the hydrogen at C-5 in **23**. This is a secondary position, and if the intermediate generated is carbene **11**, it has an allylic stabilization energy. Assuming there is no significant perturbation of the bond energy for this bond by the first radical center, the C-5 C–H bond energy is calculated[24] to be +84 kcal/mol. Recombining the two hydrogen atoms to return them to the standard state releases the H_2 bond energy (104 kcal/mol). This gives 87.6 + 84 − 104 = +68 kcal/mol as the estimated heat of formation of carbene **11**. If we assume that the biradical **10** lacks the allylic stabilization present in **11** (*cf.* Scheme I), it presumably has an energy 10–11 kcal higher than **11**.

Combining these energies with the activation energy for racemization of **9** (which corresponds to the height of the barrier which must be crossed to reach the intermediate) generates the reaction coordinate diagram illustrated in Figure 1. This shows that while the heat of formation of **11** is lower than that of the transition state, the heat of formation of **10** is higher. Therefore, if the thermochemical analysis is correct, biradical **10** cannot be an intermediate in the cyclopropene pyrolysis, but carbene **11** can. We therefore feel that the most likely mechanism for ring opening is some combination of ring cleavage and rotation occurring simultaneously leading directly from **9** to **11**.

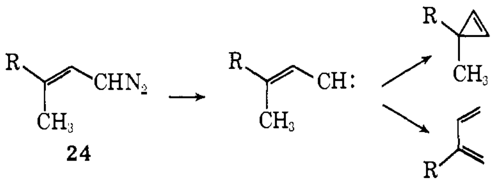
It would be quite interesting to know whether this sort of energy surface would be predicted by reliable quantum chemical calculations. Unfortunately, despite the fact that cyclopropene–vinylcarbene is a very convenient system in which to carry out such theoretical calculations (it has many fewer critical internal degrees of freedom than does cyclopropene–trimethylene), there appears to be no report of such work in the literature. It is our hope that this situation will be corrected in the near future.

Assuming that there is one intermediate in this reaction, its behavior can be described in terms of the kinetics shown in Scheme VIII. This is a special (and simplified) case of a more general kinetic system which we analyzed earlier in attempting to understand the kinetics of geometric isomerization and racemization of 1-methyl-2-ethylcyclopropane.[3e] Using that analysis, within the limits of the steady-state assumption, the rate of reclosure of **11** to cyclopropene (k_{-1}) relative to that for product formation (k_2) is simply equal to the ratio of unimolecular rate constants $k_{\mathrm{DL}}/k_{\mathrm{P}}$. Thus the intermediate **11** is predicted to undergo "rotating ring closure" about nine times faster than it goes on to products.

Scheme VIII

$$\begin{tikzcd}
\mathbf{9a} \arrow[r, shift left, "k_1"] & \mathbf{11} \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_{-1}"'] \arrow[d, "k_2"] & \mathbf{9b} \arrow[l, shift left, "k_1"'] \\
 & \text{products} &
\end{tikzcd}$$

There are two important comments we wish to make about this conclusion. First, in a qualitative sense, it appears to be consistent with Closs' observations[7a,b] on the decomposition of vinyl diazo compounds (*e.g.*, **24**).



Such decompositions, which presumably pass through vinylcarbenes related to **11**, give almost completely cyclopropene products.[7a,b] Thus the intermediate generated from **24** apparently favors ring closure over hydrogen shift, just as **11** does. Unfortunately, decomposition of 5-diazo-3-heptene, the compound which should generate **11** itself, has not been examined, so we cannot make an exact comparison of the behavior of

---

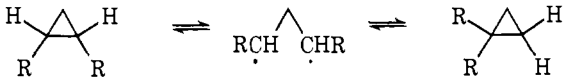
[24] Estimated using group equivalent and bond energy values given by S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[25] This method of estimating biradical heats of formation has been used extensively by Benson and coworkers; *cf.* H. E. O'Neal and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970), and references cited therein.

the intermediate generated from the diazo compound with that generated from 1,3-diethylcyclopropene. However, the qualitative comparisons which can be made between similar, if not identical, systems suggest that vinyl diazo compounds and cyclopropenes may well decompose through the same intermediates.[26]

Second, we believe that our kinetic results are relevant to the question posed in the introduction to this paper concerning strain-generated barriers to ring closure in small-ring biradicals. Despite the fact that **11** must sacrifice both an allylic resonance energy and 54 kcal/mol of strain energy in order to re-form diethylcyclopropene, it still exhibits a cyclization/product formation ratio only a factor of three different[3b] from that of the trimethylene biradical (**2**). We see no reason to expect much difference in the rate constants for hydrogen shift in intermediates **2** and **11**, and so we believe these results strongly suggest that the absolute rate constants for ring closure are similar in **11** and in trimethylene. One way to account for this, of course, is to accept the suggestion of quantum mechanics[5] that barriers to ring closure are nonexistent, and thus might well not be perturbed by structural changes. In any case, if such barriers do exist, our results strongly indicate that they cannot have the onset of ring strain as their source.

Substituent Effects. Mention should be made here of the unusual effect of substituents on the energy required for cyclopropene pyrolysis. It is well known that alkyl and vinyl substituents stabilize free radicals, and thereby lower carbon–carbon bond energies in saturated three-membered rings.[27a,b] For example, *cis*-1,2-dimethylcyclopropane (**25C**) undergoes cis,trans isomerization with an activation energy of 59 kcal/mol;[27c] this is 5 kcal/mol less than that required for stereoisomerizing 1,2-dideuteriocyclopropane (**4**). Thus the energy of the transition state leading to biradical **27** reflects a roughly 2 kcal/mol stabilization of each radical center by a methyl group. Attempting to transfer this effect to the cyclopropene system causes some difficulties. Alkyl-substituted cyclopropenes all decompose with activation energies in the range 30–40 kcal/mol,[20] but it is somewhat difficult to detect a stabilizing pattern in the influence of alkyl substitution on activation energy; in fact, a case has been made that such substitution may strengthen the single bond in the cyclopropene ring.[20b] Pyrolyses of unsubstituted or minimally substituted cyclopropenes, however, are known to be complicated by serious surface effects,[20] and so small differences in activation energies may not be terribly reliable. If the alkyl effect actually is destabilizing or nonexistent, one important consequence will be to modify our calculated $\Delta H_f°$ for carbene **11**. In making that estimate, we assumed that a vinyl C–H bond was weakened some 3 kcal/mol by an attached alkyl group. To the extent that the attached ethyl group does *not* stabilize the intermediate, the carbene will be higher in energy and find itself in a correspondingly shallower energy well. This would again strengthen the prediction of a negligible diradical ring-closure barrier in **11**.

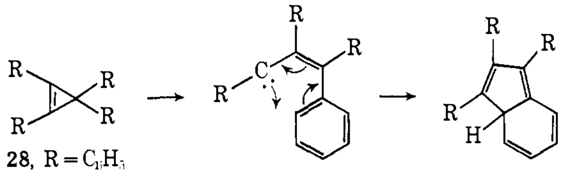


4C, R = D
25C, R = CH_3
26C, R = C_6H_5

27

4T, R = D
25T, R = CH_3
26T, R = C_6H_5

A comparison of the effect of phenyl substitution on cyclopropane and cyclopropene pyrolyses is even more dramatic. 1,2-Diphenylcyclopropane (**26**) undergoes stereoisomerization with an activation energy of 35 kcal/mol,[28] which suggests that each phenyl group lowers the barrier to ring cleavage by about 12–13 kcal/mol relative to 1,2-dimethylcyclopropane.[29] Were this effect to operate in the cyclopropene system, tetraphenylcyclopropene (**28**) should undergo ring opening with an activation energy of about 35 − 2(12) or 11 kcal/mol. Unfortunately, a racemization experiment on an appropriately substituted tetraarylcyclopropene has not been carried out, but Battiste, Halton, and Grubbs have examined the products formed on pyrolysis of a number of racemic derivatives.[30] These molecules rearrange to isoindenes (**30**), presumably *via* intermediates (**29**) much like the ones we have been discussing for the pyrolysis of **9**.[31] Battiste and coworkers report that rearrangement takes place with E_a = 40 kcal/mol! Clearly, phenyl groups affect the C–C single bond energies in cyclopropene rings in a strikingly unprecedented manner.



28, R = C_6H_5

29

30, R = C_6H_5

Experimental Section

Optical rotations were determined on a Perkin-Elmer 141 digital readout polarimeter, nuclear magnetic resonance (nmr) spectra on Varian Associates A-60 and HR-220 spectrometers, and infrared (ir) spectra on a Perkin-Elmer 257 instrument. Mass spectra were determined on an EAI Quad. 300D instrument. Microanalyses were performed by Spang Microanalytical Lab, Ann Arbor, Mich.

Vapor phase chromatography (vpc, glc) was carried out on Hewlett-Packard and Varian instruments (see below). In the experimental text the numbers of the glc columns listed below are given, followed by parentheses with the flow rate in ml/min (or flow meter reading), the temperature in °C, and the model used for the analysis. Models used: HP = Hewlett-Packard Model 17503A

---

[26] 3,3-Dimethylcyclopropene, on pyrolysis in olefin solution, gives a cyclopropane product which can be understood to have arisen by addition of 2-methylpropenylcarbene to the olefin; Professor G. L. Closs, private communication.

[27] (a) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); S. W. Benson and H. E. O'Neal, NSRDS-NBS Monograph No. 21, 1970, pp 223 ff; (c) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc., Ser. A*, **257**, 122 (1960).

[28] (a) L. B. Rodewald and C. H. DePuy, *Tetrahedron Lett.*, 2951 (1964); (b) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968).

[29] An additional phenyl group seems to provide no further weakening of the cyclopropane ring bond (*cf.* ref 30); models indicate that two phenyl rings attached to the same radical carbon atom would encounter serious steric repulsion if both were properly oriented for maximum stabilization of the radical.

[30] M. A. Battiste, B. Halton, and R. H. Grubbs, *Chem. Commun.*, 907 (1967).

[31] 1,2,3-Triphenyl-3-vinylcyclopropene apparently behaves similarly, rearranging to 1,2,3-triphenylcyclopentadiene at the same temperature required for the rearrangement of 28; *cf.* R. Breslow in "Molecular Rearrangements," P. DeMayo, Ed., Vol. I, Interscience, New York, N. Y., 1963.

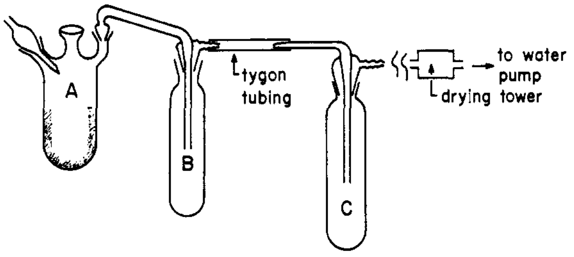


Figure 2. Apparatus used for pyrolysis of *trans*-2,3-diethylcyclopropyltrimethylammonium hydroxide (**14**).

equipped with a Model 3370A digital integrator; VA = Varian aerograph Model A-90-P3.

If not indicated otherwise, stainless steel tubing was used for columns. Columns employed: column 1, 6 ft × 0.25 in. 5% SE-30 on 42–60 Chromosorb G; column 2, 5 ft × 0.25 in. 3% SE-30 on 100–120 Varaport 30; column 3, 10 ft × 0.25 in. 10% UC-W 98 (glass) on 100–120 Chromosorb W, AW; column 4, 10 ft × 0.25 in. 10% SE-30 on 60–80 Chromosorb P, NAW; column 5, 10 ft × 0.25 in. 20% SE-30 on 60–80 Chromosorb P, NAW; column 6, 10 ft × $^1/_8$ in. 8% UC-W98 on 60–80 Chromosorb W, AW; column 7, 15 ft × $^3/_8$ in. 10% UC-W98 on 100–120 Chromosorb W, AW; column 8, 15 ft × $^1/_8$ in. 25% ββ; ODPN on 100–120 Chromosorb P, NAW; column 9, 19.75 ft × 0.25 in. 25% ββ′ ODPN on 100–120 Chromosorb P, NAW.

(±)-*trans*-2,3-Diethyl-1-methylaminocyclopropane. To a solution of 55.5 g of **12** (0.385 mol) in 65 ml of H_2O and 150 ml of acetone (2-l. three-necked flask, stirrer, inner thermometer, dropping funnel), cooled to 0°, a solution of 45.5 g (0.45 mol) of triethylamine in 790 ml of acetone was added within 15 min; max temp, 5°. At −3 to +1° 56 g (0.515 mol) of ethyl chloroformate[32] in 200 ml of acetone was then added dropwise (~1 hr) and stirring continued for 0.5 hr at 0°.

Subsequently, 37.8 g (0.58 mol) of sodium azide in 135 ml of H_2O was added slowly (35 min, 0°) and the mixture stirred an additional 90 min. The solution was poured into 1.5–2 l. of ice-water and extracted three times with ether, and the ether layer was washed with brine and dried over $MgSO_4$. After removal of the solvent at 25° (~30 mm), 73 g of a light yellow product was obtained, which showed a strong azide band in the ir (in CCl_4), 2145 (azide) and 1710 (carbonyl) cm^{-1}. The crude azide, dissolved in 150 ml of dry benzene, was added slowly to boiling benzene (200 ml) during 75 min; smooth N_2 evolution occurred. The reaction was monitored by ir, showing the disappearance of the azide band. Reflux was continued for 5.75 hr; during the last 3 hr the ir did not change.

Benzene was removed (60–70° (20–30 min)) and 47 g of crude isocyanate obtained; ir (CCl_4) 2180 cm^{-1} (isocyanate). The product was dissolved in dry ether and added to a suspension of 19 g (0.5 mol) of $LiAlH_4$ in 800 ml of dry ether at such a rate that slight reflux was maintained. After additional reflux for 1.5 hr the mixture was allowed to remain at room temperature for 1 hr and cooled with ice to 5°; 450 ml of ice-water and 350 ml of cold concentrated HCl were added at 5–12°. The resulting yellow solution was extracted two times with ether, and the water layer was made alkaline with KOH pellets (up to pH ~8); formation of a voluminous white precipitate was observed. Extraction with ether was difficult because phase separation turned out to be insufficient. The whole mixture was filtered by suction, the precipitate washed and shaken several times with ether, and the filtrate treated likewise. After drying over anhydrous K_2CO_3 overnight and removal *in vacuo*, 28 g of crude material was obtained, which upon distillation gave 23.5 g of product (47%, based on acid **12**), colorless liquid, bp 45–50° (22–25 nm). Glc analysis of four fractions, column 2 (100 ml/min, 85°, VA), indicated that only one major product was present, along with traces of ether and other impurities.

When an aliquot of the liquid was allowed to stand at room temperature in an open bottle, it transformed to white crystals, the nmr being identical with that of the liquid (hydrate formation?). Without further purification the amine was used for the following step. Nmr (CCl_4): δ (ppm) 0.1–0.7 (2 H, m, H_2, H_3), 0.8–1.55 (~10 H, m, ethyl), 1.77 (1 H, m, H_1), 2.38 (3 H, s, methyl).

(±)-*trans*-2,3-Diethyl-1-dimethylaminocyclopropane. To 21.6 g (0.17 mol) of (±)-*trans*-2,3-diethyl-1-methylaminocyclopropane, 40 g of formic acid (0.85 mol; 98–100% pure) was slowly added (10 min) at 0°. A 37% solution of formaldehyde in water (38 ml) was then added at once and the mixture was heated to 80–90°; CO_2 evolution started immediately and the oil bath was removed. When the gas evolution had diminished, heating to reflux was continued for 3.5 hr; the nmr spectrum of an aliquot, taken after 2.5 hr and worked up as described below, showed the absence of starting material. Work-up: cooling of the reaction mixture with ice, addition of 50 ml of 4 *N* HCl (pH 1–2), concentration at reduced pressure, addition of 60 ml of ~50% NaOH solution (pH >8) under cooling, extraction of the water phase three times with ether, and drying over anhydrous K_2CO_3 overnight. The solvent was removed *in vacuo* and the light yellow residue distilled; three fractions were obtained, a total of 17.3 g (72%), water white liquid: bp 50–51° (20 mm); ir (CCl_4) no absorption between 1500 and 2700 cm^{-1}; nmr (CCl_4) δ (ppm) 0.05–0.7 (2 H, m, H_2, H_3), 0.7–1.8 (11 H, m, ethyl, H_1), 2.2 (6H, s, dimethylamino).

(±)-*trans*-2,3-Diethylcyclopropyl-1-trimethylammonium Iodide (14). Colorless methyl iodide, 24.6 g (0.17 mol), was added at room temperature within 5 min to a stirred solution of 16.2 g (0.11 mol) of (±)-*trans*-2,3-diethyl-1-dimethylaminocyclopropane in 20 ml of absolute ethanol under argon. Glc analysis, column 2 (100 ml/min, 83°, VA) of an aliquot, taken after 60 hr, indicated that the amine had been completely consumed. The solution was warmed to 40°, ether (~15 ml) added until crystallization started, and mixture maintained at room temperature for 3 hr and at 5° overnight. Nearly colorless crystals (21 g), mp 188–189°, were collected. A second crop could be obtained by adding 40 ml of ether and seed crystals to the mother liquor at 40° and cooling slowly (otherwise two layers separate) to room temperature, 5°, and finally to −10°. Material (8 g), mp 187–189°, was obtained: total yield, 93%; nmr (D_2O, external TMS) δ (ppm) 0.8–2.2 (12 H, m), 3.2–2.8 (1 H, broad m), 3.20 (9 H, s). *Anal.* Calcd for $C_{10}H_{22}NI$: C, 42.40; H, 7.83; N, 4.94. Found: C, 42.33; H, 7.78; N, 4.91.

(±)-1,3-Diethylcyclopropene (9). Iodide **14** (7.1 g, 0.025 mol) and 11.5 g (0.05 mol; reagent quality product from Mallinckrodt) of silver oxide were combined in 60 ml of H_2O, stirred under nitrogen for 5.25 hr at room temperature, and stored at −18° overnight. After filtration a clear solution of hydroxide **15** was obtained showing no precipitate when a $AgNO_2$–HNO_3–H_2O solution was added to an aliquot. Half of the solution was concentrated at ~40° (0.3 mm) to a volume of 6–10 ml. Pyrolysis was performed in the apparatus shown in Figure 2. The inner walls of reaction vessel A were covered with 20% platinum on asbestos (from Engelhard Chemicals and Catalysts, New York) 1–3 mm thick. After flushing the apparatus with argon, a gas capillary tube, connected to an argon cylinder equipped with a bubbler, was introduced in flask A and the system evacuated by means of a water pump (25–30 mm). Flask A was then immersed in a bath of a molten KNO_3–$NaNO_3$ mixture (heated to 360°) to a level of ~45 mm; traps B and C were cooled with liquid nitrogen. Subsequently, the concentrated solution of **15**, cooled to 0°, was injected dropwise through the septum of flask A with a 250- or 1000-μl syringe in quantities from 250 to 500 μl; the syringe was turned during the injections so that the drops reached different areas of the hot vessel. The pressure remained constant during all operations.

Pentane was added to the trapped products (most of which were caught in flask B), the water layer was frozen with Dry Ice, and the organic phases were taken off with a pipet. Glc analysis, column 5 (80 ml/min, 100°, VA), gave a rough estimate of the product distribution: 15–25% **9**, 10–15% other hydrocarbons, 60–75% recovered amine. The combined pentane solutions were extracted at 0° with a 10% HCl solution, quickly separated, twice washed with ice-water (the last water phase was neutral), and dried over Na_2SO_4. No amine could be detected in the pentane solution by glc.

The cyclopropene was purified by preparative glc, column 7 (100 ml/min, room temperature, VA), and was obtained in ~12% yield based on iodide **14**; impurities ≤2% by glc. It had a parent peak in the mass spectrum at *m/e* 96, and the methylene hydrogens at C-3 were shown to be diastereotopic by nmr: (220 mHz, CCl_4) δ 0.79 (3 H, t, *J* = 7.5 Hz), 1.14 (3 H, t, *J* = 7.5 Hz), 1.31 (2 H, m), 1.42 (1 H, d of t, *J* = 5.0, 1.6 Hz), 2.44 (2 H, d of q, *J* = 7.5, 1.1 Hz), 6.56 (1 H, br s) ppm. The material polymerizes slowly at room temperature and must be stored at −78°.

Flow Pyrolysis of (±)-1,3-Diethylcyclopropene (9). At a nitrogen flow rate of 80 ml/min, a solution containing 120 mg of **9** (1.24 mmol) in ~1 ml of *n*-pentane was pyrolyzed in a conventional atmospheric pressure flow system.

---

(32) J. Weinstock, *J. Org. Chem.*, 26, 3511 (1961).

Glc analysis of the trapped pentane solution, column 6 (HP; 25°), showed nearly quantitative disappearance of the starting material; the products were formed in *ca.* 40% yield (based on glc analysis). The products are poorly resolved on column 6 (room temperature), but appear as three symmetrical peaks using column 8 (40°).

Three fractions were isolated by preparative glc, column 9 (100 ml/min; room temperature; VA), and identified as described in the text. The first pyrolysis fraction (34%) was found to be pure **16**, the second (37%) contained about a 10:1 ratio of **18** and **19**, and the third was identified as pure **17**.

Alternative Synthesis of (±)-*trans*-2,3-Diethylcyclopropyl-1-trimethylammonium Iodide (14). A mixture of 5.0 g (0.035 mol) of **12** and 25 ml (~0.35 mol) of thionyl chloride was stirred at room temperature for 1 hr. Distillation of the excess thionyl chloride under aspirator vacuum left a pale brown liquid which was dissolved in 100 ml of dry acetone and cooled in an ice bath. To this was added with rapid stirring 3.25 g (0.05 mol) of sodium azide dissolved in a minimum amount of H_2O. The mixture was stirred for 1 hr, then poured into H_2O and extracted with ether. After drying over $MgSO_4$, the ether solution was added dropwise to 125 ml of refluxing benzene. The ether was allowed to distill over. The benzene solution was refluxed until an ir of an aliquot showed no $-N_3$ absorption at 2160 cm^{-1}. The benzene was removed on the rotary evaporator leaving the isocyanate. This was refluxed with 100 ml of 10% HCl for 5 hr. All solvent was removed on the rotary evaporator and the residue was dissolved in 50 ml of H_2O and extracted with ether. The aqueous layer was made strongly basic with 10 *N* NaOH and extracted twice with ether. The combined ether extracts were dried over $MgSO_4$, and, after removal of the ether on the rotary evaporator, left 1.48 g (37%) of (±)-*trans*-2,3-diethylcyclopropylamine (**13**). Nmr after bulb-to-bulb distillation (CCl_4): τ 7.98 (1 H), 8.2–9.5 (m, 12 H), 9.5–1.0 (m, 2 H); ir (cm^{-1}) 3380 (broad, w), 2960 (s), 2920 (s), 2880 (s), 2720 (s), 1610 (m), 1620 (m), 1460 (s), 1470 (s).

A mixture of 565 mg (5 mmol) of amine **13**, 1.26 g (15 mmol) of sodium bicarbonate, and 2.13 g (15 mmol) of methyl iodide in 20 ml of MeOH was refluxed with stirring for 3 days. An additional 1.14 g (8 mmol) of methyl iodide was added in two portions. All solvent was removed on the rotary evaporator and the white solid remaining was extracted with three 20-ml portions of boiling $CHCl_3$. The combined cooled $CHCl_3$ extracts were filtered from a white precipitate (NaI) and the $CHCl_3$ was removed from the filtrate on the rotary evaporator. Two crystallizations of the residue from 2-propanol–hexane gave 132 mg of **14** (9.3%), mp 189–190°. A second crop gave 183 mg (13%), mp 188–189°. The nmr was identical with that of a sample prepared according to the route described above.

Optically active 1,3-diethylcyclopropene (9) was synthesized from optically active cyclopropane precursors as described below using procedures identical with those used to prepare the racemic materials. Structural identity of active and racemic compounds was established in each case by comparison of the nmr and/or vpc behavior of both materials.

(−)-*N*-Methyl-*trans*-2,3-Diethylcyclopropylamine was prepared as described for the racemic material by $LiAlH_4$ reduction of the isocyanate prepared from a sample of (−)-*trans*-2,3-diethylcyclopropanecarboxylic acid[17] of rotation $[\alpha]^{25}_{\mathrm{D}}$ −4.8°, $[\alpha]^{25}_{365}$ −6.45° (*c* 0.0312, 95% EtOH). The amine was obtained in 30% distilled yield and had a rotation of $[\alpha]^{25}_{\mathrm{D}}$ −13.8°, $[\alpha]^{25}_{365}$ −45.6° (*c* 0.0221, CCl_4). **(−)-*N*,*N*-Dimethyl-*trans*-2,3-diethylcyclopropylamine** was obtained from the monomethylamine in 74% yield; its rotation was $[\alpha]^{25}_{\mathrm{D}}$ −52.0°, $[\alpha]^{25}_{365}$ −151.0° (*c* 0.0247, EtOH). Quaternization of the dimethylamine in 94% yield gave **(−)-*trans*-2,3-diethylcyclopropyltrimethylammonium iodide (14)**, $[\alpha]^{25}_{\mathrm{D}}$ −45.5° (*c* 0.0386, H_2O (cloudy solution)). Conversion to the quaternary hydroxide **15** followed by pyrolysis at 360° on Pt/asbestos gave 14% of **(+)-1,3-diethylcyclopropene (9)**, purified by preparative vpc. It had a rotation of $[\alpha]^{25}_{\mathrm{D}}$ +34.0°, $[\alpha]^{25}_{365}$ +119.0° (*c* 0.0050, CCl_4), $[\alpha]^{25}_{\mathrm{D}}$ +32.4,° $[\alpha]^{25}_{365}$ +115.7° (*c* 0.0050, MeOH).

In a similar fashion, a sample of (+)-*trans*-2,3-diethylcyclopropanecarboxylic acid, $[\alpha]^{25}_{\mathrm{D}}$ +2.24,° $[\alpha]^{25}_{365}$ +2.56° (*c* 0.0313, EtOH), gave the following optically active derivatives.

(+)-*N*-Methyl-*trans*-2,3-diethylcyclopropylamine: 44.5%; $[\alpha]^{25}_{365}$ +22.2° (*c* 0.0227, CCl_4).

(+)-*N*,*N*-Dimethyl-*trans*-2,3-diethylcyclopropylamine: 88%; $[\alpha]^{25}_{\mathrm{D}}$ +30.0°, $[\alpha]^{25}_{365}$ +81.0° (*c* 0.0227, EtOH).

(+)-*trans*-2,3-Diethylcyclopropyltrimethylammonium iodide: 90%; $[\alpha]^{25}_{\mathrm{D}}$ +13.9° (*c* 0.0244, H_2O).

(−)-1,3-Diethylcyclopropene (9): run A, 17%, $[\alpha]^{25}_{\mathrm{D}}$ −16.2°, $[\alpha]^{25}_{365}$ −52.6° (*c* 0.0069, MeOH); run B, 16%, $[\alpha]^{25}_{\mathrm{D}}$ −18.8°, $[\alpha]^{25}_{365}$ −55.9° (*c* 0.0072, MeOH); run C, 19.6%, $[\alpha]^{25}_{\mathrm{D}}$ −18.2°, $[\alpha]^{25}_{365}$ −53.9° (*c* 0.0074, MeOH).

Kinetics of Pyrolysis of 9. Two sampling techniques were used. Studies on racemic material employed an aliquot method in which consecutive portions of material in the lead–alkaline glass reactor were removed and condensed in liquid N_2 at specific time intervals. An internal standard, methylcyclopentane, was vaporized along with the cyclopropene into the reactor and pentane vapor was added to bring the pressure to 60–65 mm in the bulb. Pentane was added to each condensed aliquot and the aliquots were analyzed for the cyclopropene, standard, and products on a Hewlett-Packard 5750 vpc using column 6 at room temperature. The aliquots were stored in Dry Ice and prior to use were warmed to room temperature. The injection technique employed a 10-μl syringe filled with 1 μl of air, 1 μl of pentane, 1 μl of air, and 1–2 μl of sample, all at room temperature. Analyses of each aliquot gave an average deviation of the mean of the ratio of the cyclopropene to standard or of the cyclopropene to cyclopropene-plus-products of less than 3%.

A different sampling method was used in the pyrolysis of optically active material in order to obtain enough sample after reaction to measure the optical rotation. For each of the points obtained during a rate constant determination (P_{total} = 15–40 mm), all of the material in the bulb was condensed out after a known amount of time. Internal standard and pentane were omitted. A portion of the condensed sample was weighed into a 1-ml volumetric flask and dissolved in MeOH to exactly 1.00 ml. The optical rotation of the solution was measured, pentane was added to the remainder of the sample, and product analyses were performed on the HP 5750 as described above.

The effect of changing surface/volume ratio was examined by carrying out pyrolyses of both racemic and optically active **9** in a seasoned lead–alkaline glass reaction vessel packed with small tubes made of the same material (a surface/volume increase of 7:1). Rate constants k_α and k_i obtained in this way were within experimental error of those measured in the unpacked reactor.

Acknowledgments. We are grateful to the National Science Foundation for financial support of this work and to Professor G. L. Closs for stimulating discussions.