yield obtained was approximately the same but the oxidation time was shorter (15 min). Pyrazolidine and 4-methylpyrazolidine were best handled by this method because of their limited solubility in pentane.

(c) Oxidation by Molecular Oxygen in the Presence of Cupric Acetate. Cupric acetate (0.5 g) was added to a methanol solution of the pyrazolidine (0.4 mole) and the solution was stirred rapidly under oxygen for 90 min at room temperature. The reaction mixture was then diluted with ether and dried over anhydrous sodium sulfate. Distillation of the mixture gave a 71% yield in the case of 1-pyrazoline.

Acknowledgments. The authors are grateful to the Petroleum Research Fund of the American Chemical Society (Grant 1770-A4) and to the National Research Council of Canada for support of this work.

The Mechanism of the Thermal Decomposition of 1-Pyrazolines and Its Relationship to Cyclopropane Isomerizations[1]

Robert J. Crawford and Anupama Mishra[2]

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada. *Received April 9, 1966*

Abstract. The kinetics and products of pyrolysis of ten different pyrazolines are described. The pyrolysis of 4-methyl-1-pyrazoline-4-d_1 demonstrates the existence of an intermediate, during pyrolysis, that gives rise to olefin and cyclopropane. The intermediate, on the basis of kinetic evidence, is nitrogen free. A structure is suggested for the intermediate that is capable of explaining the stereochemistry of the olefins and cyclopropanes produced. Evidence is provided that the same intermediate plays a role in the isomerization of cyclopropanes to alkenes.

It is the purpose of this paper to (a) describe the kinetics of the gas phase thermal decomposition of a series of 1-pyrazolines, (b) present evidence for the existence of an intermediate, and (c) compare the product compositions, where possible, with those of cyclopropane pyrolysis. The 1-pyrazoline system was chosen in that the extrusion of nitrogen, by analogy with the decomposition of azoalkanes, is expected to produce a 1,3 diradical, an intermediate frequently suggested for the thermal conversion of cyclopropane to propylene.[3]

Experimental Section

Materials. The 1-pyrazolines utilized were prepared as described in the preceding paper.[4] Each sample was carefully purified by preparative gc using a 20-ft Ucon-insoluble on Diatoport column. They were then subjected to a single trap-to-trap distillation to rid them of traces of contaminants from the column.

4-Methyl-1-pyrazoline-4-d_1. This compound was prepared essentially as in the preceding paper,[4] except that 2-methyl-1,3-dibromopropane-2-d_1 was prepared by adding deuterium bromide to α-methallyl bromide in the presence of peroxides as described by Brewster.[5] Careful integration of its nmr spectrum revealed that the compound contained $17 \pm 3\%$ protium at C_4.

Kinetic Measurements. The reactor system was essentially that designed by Smith, *et al.*[6] The procedure adopted was also the same. Benzene was used as a solvent for 4,4-dimethyl-1-pyrazoline and 2,3-diazobicyclo[2.2.1]heptene. The other samples being liquid were injected neat or with cyclohexene. The thermocouple used for temperature measurements was a four-junction Chromel–Alumel type with an ice-water reference junction, and was calibrated against roll sulfur, tin (analytical), and lead (analytical).

Product Identification. Analysis of the hydrocarbons produced was carried out on the appropriate gc columns; samples were trapped and checked by mass spectrometry using an AEI MS-2-H mass spectrometer with an ionizing potential of 70 v. The retention time of each fraction was checked on two different gc columns and their infrared spectra were taken using a Perkin-Elmer Model 421 spectrometer, all data being compared with those of authentic samples. The exact product compositions were obtained by sealing degassed samples (~1 mg in size) in small Pyrex bulbs which were heated for 5 half-lives at the appropriate temperature. The bulbs were then broken inside a heated port through which carrier gas was allowed to flow; thus all the products were carried into the chromatographic apparatus.[7] Almost all of the products could be analyzed accurately on an 20-ft column of 25% silver nitrate–saturated 1,3-propanediol on firebrick. Nitrogen and cyclopropane, however, were more suitably measured on an 8-ft column of 20% *n*-butyl maleate on Fluoropak. A tandem arrangement consisting of the previously mentioned silver nitrate column and a 6-ft 10% tritolyl-orthophosphate on Chromosorb was required to resolve 2-methyl-1-butene from 3-methyl-1-butene. Gas volumes, for gc calibration, were measured using a Toeppler pump.

Control Run Using 7. A sample of 7 was injected into the reactor and allowed to react to 1 half-life. The reactor was then pumped out, and those materials condensable on the vacuum line at 0° were submitted for an nmr spectrum. 6 could be detected in this manner, and only 7 was observed to be present. The total absence of *cis*-2-pentene during the pyrolysis of 6 also indicates that 6 is not converted to 7.

Results

Kinetics. Table I gives the rate constants calculated for each of the compounds studied at five temperatures along with the kinetic parameters obtained by a least-

---

[1] Some of these observations were reported earlier as a communication: R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3768 (1965).

[2] Taken in part from the Ph.D. thesis of A. Mishra, submitted to the University of Alberta, Edmonton, 1965. National Research Council of Canada Scholarship Holder, 1964–1965.

[3] (a) D. W. Setser and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **86**, 564 (1964); (b) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958); (c) A. T. Blades, *Can. J. Chem.*, **39**, 140 (1961); (d) J. P. Chesick, *J. Am. Chem. Soc.*, **82**, 3277 (1960); (e) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3953 (1959); (f) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 18 (1962).

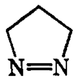
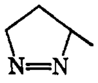
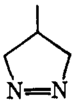
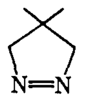
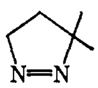
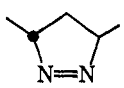
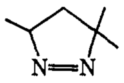
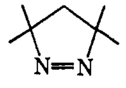
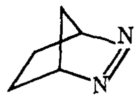
[4] R. J. Crawford, A. Mishra, and R. J. Dummel, *J. Am. Chem. Soc.*, **88**, 3959 (1966).

[5] J. H. Brewster, *ibid.*, **73**, 366 (1951).

[6] G. G. Smith and F. D. Bagley, *Rev. Sci. Instr.*, **32**, 703 (1961).

[7] C. Steel, *J. Phys. Chem.*, **67**, 1779 (1963).

Table I. Rate Constants and Kinetic Parameters from the Pyrolysis of 1-Pyrazolines at 100–200 mm

Compound	Temp, °C	10^4k, sec^{-1}	E_a, kcal $mole^{-1}$	−Log A	ΔS^*_{250}, eu
 **1**	202.0	2.28[a]	42.4 ± 0.3	15.93 ± 0.13	11.2 ± 0.6
	210.6	5.02			
	214.3	6.95			
	223.0	15.9			
	237.3	50.5			
 **2**	190.5	2.02	41.0 ± 0.3	15.70 ± 0.15	10.1 ± 0.7
	203.1	6.62			
	208.0	10.1			
	219.0	28.1			
	230.0	65.6			
 **3**	199.5	1.84	42.2 ± 0.2	15.85 ± 0.05	10.8 ± 0.3
	212.5	6.14			
	222.1	14.6			
	224.9	18.2			
	234.5	41.1			
 **4**	247.5	1.23	42.8 ± 0.2	14.10 ± 0.07	2.9 ± 0.3
	253.0	1.8			
	270.3	7.1			
	281.7	16.1			
	286.1	21.3			
 **5**	184.2	4.55	40.0 ± 0.2	15.85 ± 0.03	10.8 ± 0.2
	188.0	6.54			
	191.0	8.74			
	204.0	28.7			
	211.4	54.2			
 **6**	191.0	3.03	40.3 ± 0.3	15.54 ± 0.11	9.4 ± 0.5
	196.5	5.31			
	205.8	11.8			
	271.6	33.7			
	224.0	56.3			
 **7**	181.0	1.84	40.2 ± 0.3	15.67 ± 0.11	10.0 ± 0.5
	190.0	4.44			
	197.0	8.06			
	207.0	20.7			
	220.3	64.4			
 **8**	183.6	5.90	39.0 ± 0.4	15.42 ± 0.21	8.4 ± 0.9
	196.0	17.1			
	201.5	27.7			
	212.0	71.9			
	215.1	92.8			
 **9**	176.6	1.29	37.7 ± 0.4	14.49 ± 0.12	4.6 ± 0.8
	189.5	4.49			
	197.5	8.24			
	205.0	15.8			
	219.3	52.0			
 10	171.0	3.37	36.9 ± 0.2	14.74 ± 0.10	5.8 ± 0.5
	177.2	6.02			
	183.0	10.1			
	190.5	19.0			
	202.4	53.5			
			37.3 ± 0.3[b]	14.90 ± 0.10[b]	6.3 ± 0.5[b]

[a] Initial pressures of 50, 100, and 350 mm gave the same rate constant within 3%. [b] See ref 8.

squares treatment of the data. The largest error is derived from difficulty in maintaining a constant high temperature for a long period of time; thus the temperature of slow runs may vary from start to finish by as much as a tenth of a degree. The over-all precision in each run is excellent as indicated by the example run in Table II and Figure 1. The rate constants were obtained by reading the transducer emf off a strip-chart recorder and plotting log ($E_\infty - E_t$) *vs.* t, where E_∞ is the transducer emf after more than 7 half-lives and E_t is the emf at time t in seconds.[6] The rate constant is thus obtained from the slope with high precision since a large number of points can be obtained from the chart record. Generally 20 points were used and the values were taken at regular intervals over the first 2 half-lives of the reaction. The plots remained linear when the reaction was followed to greater than 95% completion. The kinetics of pyrolysis of pyrazoline **10** have previously been described in the literature,[8] and they were duplicated here to test the validity of the method (see

---

[8] S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961).

Table I). The rate of **3** was also followed gas chromatographically using a sealed glass ampoule containing a definite amount of **3** as delivered by a microsyringe.

Table II. Sample Kinetic Run of 2,3-Diazabicyclo[2.2.1]hept-2-ene(**10**)[a] at 183.0 ± 0.1°

t, min	E_t	Log $(E_\infty - E_t)$	t, min	E_t	Log $(E_\infty - E_t)$
2	186	1.9138	12	224	1.6435
3	192	1.8808	13	226	1.6232
4	196	1.8573	14	229	1.5911
5	200	1.8325	15	232	1.5563
6	204	1.8062	16	234	1.5315
7	208	1.7782	17	236	1.5051
8	212	1.7482	18	238	1.4771
9	215	1.7243	19	239	1.4624
10	218	1.6990	20	241	1.4314
11	221	1.6721	21	242	1.4065
		$k = 10.1 \times 10^{-4}$ sec^{-1}			

[a] With cyclohexane present as solvent for the injection of **10**.

The rate constant obtained by this method was 12.6 × 10^{-4} sec^{-1} at 220°, comparable to a value of 11.8 × 10^{-4} sec^{-1} extrapolated from the kinetic data. Thus the rate constant was independent of the nature of the surface, glass, or steel. The products from the pyrolysis of **1**, **6**, and **7** were checked as to their nature by both the glass-ampoule method and by analysis of the products from a kinetic run in the stainless-steel cylinder, and in each instance they were found to be independent of the nature of the surface. A check was also made of the 2-pyrazolines to see if tautomerization was of any significance. It was found, however, that these compounds decomposed only very slowly under the reaction conditions and can be discounted as playing any role in the pyrolysis of 1-pyrazolines. The decomposition of **1** using 4.3 mg (61.3 μmoles) was carried out in a glass bulb for 10 half-lives and resulted in the production of 54.0 μmoles of cyclopropane and 6.0 μmoles of propylene. Thus the hydrocarbon product totaled 60 μmoles. The error from the theoretically expected amount is 2%, which is within experimental error of the gas chromatographic technique employed.

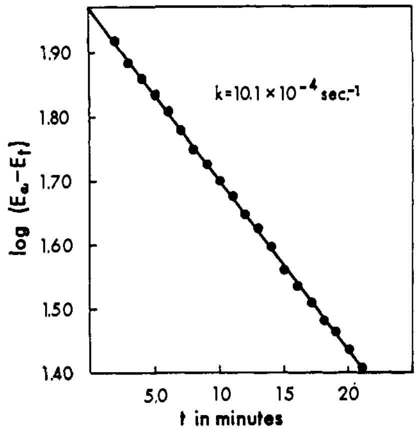


Figure 1. An example first-order rate plot from the decomposition of **10** at 183.0° and from 100 to 200 mm of pressure.

Table III. Percentage Yield[a] of Hydrocarbon Products from the Pyrolysis of 1-Pyrazolines

Pyrazoline	Temp, °C	Cyclopropane, %	Olefin, %
1	223	Cyclopropane[b] 89.2 ± 0.8	Propylene[b] 10.8 ± 0.8
2	202	Methylcyclopropane 93.3 ± 0.6	1-Butene, *trans*-2-butene 3.7 ± 0.3 1.16 ± 0.12 *cis*-2-Butene 1.9 ± 0.2
3	223	Methylcyclopropane 52.3 ± 0.4	2-Methylpropene 47.7 ± 0.4
4	249	1,1-Dimethylcyclopropane 98.6 ± 0.3	2-Methylpropene, 2-methyl-1-butene 1.4 ± 0.3 trace
5	202	1,1-Dimethylcyclopropane 96.7 ± 0.4	2-Methyl-2-butene, 3-methyl-1-butene 1.8 ± 0.2 1.5 ± 0.3
6 and 7	. . .[c]		
8	202	1,1,2-Trimethylcyclopropane 99.36 ± 0.8	2-Methyl-2-pentene, *cis*-4-methyl-2-pentene 0.24 ± 0.03 0.06 ± 0.01 *trans*-4-Methyl-2-pentene 0.34 ± 0.05
9	202	1,1,2,2-Tetramethylcyclopropane 99.75 ± 0.02	2,4-Dimethyl-2-pentene 0.25 ± 0.02
10	202	Bicyclo[2.1.0]pentane 100	Cyclopentene trace

[a] The product compositions indicated are the result of four to six determinations; the errors indicated are standard deviations. [b] Mass spectrometry gave 89.3 and 10.7%. [c] See Table IV.

Products. The products from the pyrolysis of eight of the pyrazolines are indicated in Table III, along with the percentage yields as determined by careful gas chromatographic analysis, with correction for the thermal conductivities of each hydrocarbon.[9] The *cis*- and *trans*-3,5-dimethyl-1-pyrazolines (**6** and **7**) were placed in Table IV because of their special significance in the discussion. The dependence of product proportion upon time and temperature was checked as shown in Table V. The products from the pyrolysis of 1-pyrazoline were shown to be independent of pressure in the range 50–500 mm; however, yellow oils were observed if all of the oxygen was not removed. These oils constituted less than 5% of the reaction product and were not investigated. The results in Table III

---

[9] A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, 31, 230 (1959).

are from samples which were carefully degassed and 98% of the theoretical yield was observed.

Table IV. Products of the Thermal Decomposition of 6 and 7

Pyrazolines	1,2-Dimethylcyclopropane[a]		2-Pentene	
	cis	*trans*	*cis*	*trans*
6 (*cis*)	33.2 ± 0.6[b]	66.1 ± 0.6	0.0	0.68 ± 0.08
7 (*trans*)[c]	72.6 ± 0.4	25.4 ± 0.6	0.92 ± 0.11	1.08 ± 0.17

[a] All products and reactants were checked for isomerization under the reaction conditions. [b] Average deviation as a result of six runs. [c] The same result was obtained using an optically active sample.

Table V. Product Distribution as a Function of Time and Temperature for **3**

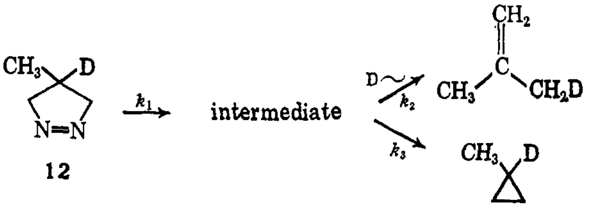
Temp, °C	Time, hr	% methylcyclopropane	% 2-methylpropene
200	2	52.0	48.0
	17	52.3	47.7
	24	52.7	47.3
		Av 52.3 ± 0.3	Av 47.7 ± 0.3
220	0.16	52.7	47.3
	0.33	51.7	48.3
	0.66	52.6	47.4
	24	52.4	47.6
		Av 52.3 ± 0.4	Av 47.7 ± 0.4
244	0.1	52.4	47.6
	0.2	52.7	47.3
	0.5	52.6	47.4
	24	52.0	48.0
		Av 52.4 ± 0.3	Av 47.6 ± 0.3

Discussion

That the 1-pyrazolines undergo unimolecular pyrolysis in the gas phase is indicated by the linearity of the first-order plots to greater than 95% completion, and by the independence of rate as a function of pressure in the range 50–350 mm for **1**. The results in Table I show that methyl substitution in the α position brings about a decrease in the activation energy for the 1-pyrazolines. The fact that the activation energies for **6** and **7** are smaller than that of **2**, and those of **8** and **9** are smaller than that of **5**, indicates that both carbon–nitrogen bonds are being cleaved in the transition state.[10] This is not a compelling argument as pre-transition-state intermediates such as **11** cannot be ruled out on kinetic grounds. However, such an intermediate is unlikely since **6** and **7** are not interconverted during their pyrolysis (see Control Run, Experimental Section). Thus it would appear that both carbon–nitrogen bonds are breaking in a simultaneous process[11] in much the manner that has been described by Seltzer[11] in the pyrolysis of azobis-α-phenylethane.[12]

(1)

The olefin yields in all of the pyrazolines except **3** are less than 11% of the hydrocarbon products; thus the kinetics of the over-all process indicates little about the olefin-forming reaction. It has generally been assumed that cyclopropane and olefin come from a common intermediate. We desired further direct proof of this and so undertook to prepare 4-methyl-1-pyrazoline-4-d_1 (**12**) on the basis that (a) the formation of methylpropene from **3** required a hydrogen shift whereas cyclopropane formation does not, and (b) that the amount of olefin produced is sufficiently large, 47.7%, that if it were being formed by an independent path then a difference in the product proportions would be expected to be reflected in the kinetics. Table VI presents kinetic and product data comparing **3** and **12**. These results are best explained on the basis of eq 2. The rate constants k_1 and k_3 are not expected to be altered by isotopic substitution at C_4 in **12**; however, k_2 would be expected to be smaller and thus more of the product would be diverted to the methylcyclopropane.



12 (2)

$k_{2H}/k_{3H} = 47.7/52.3$ and $k_{2D}/k_{3D} = 36.0/64.0$; then $k_{2H}k_{3D}/k_{2D}k_{3H} = 1.80 \pm 0.08$.

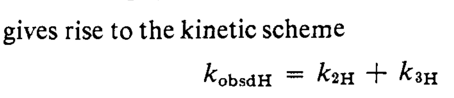
Table VI. Effect of Deuterium Substitution in **3** at 241.75°

Compd	10^4 k, sec^{-1}	% cyclopropane	% 2-methylpropane
3	64.1 ± 0.6	52.3 ± 0.3	47.7 ± 0.3
12	59.5 ± 0.6	66.0 ± 0.3	34.0 ± 0.4[a]
	k_H/k_D = 1.07 ± 0.03[a]		

[a] These results have been corrected from the observed values for 17% of **3** present in **12** as determined from a 100-Mc nmr spectrum. The methyl group in **12** consist of an equal intensity triplet at τ 9.12 (J = 0.9 cps).

If we assume that $k_{3H}/k_{3D} = 1.0$ then the magnitude of k_{2H}/k_{2D} can be calculated from the product proportions. The value obtained, 1.80, is commensurate with the value 1.59 obtained by Setser and Rabinovitch[3a] in the thermolysis of 1,2-dideuterio-3-methylcyclopropane.[13]

The alternative approach wherein olefin and cyclopropane formation occur by different paths



(3)

gives rise to the kinetic scheme

$$k_{\mathrm{obsdH}} = k_{2H} + k_{3H}$$

$$k_{\mathrm{obsdD}} = k_{2D} + k_{3D}$$

---

(10) D. M. Cameron, of this laboratory, has shown that 3-vinyl-1-pyrazoline (E_a = 32.2 kcal mole^{-1}) also undergoes a cleavage of both carbon–nitrogen bonds in the transition state by observating a kinetic isotope effect of k_H/k_D = 1.21 ± 0.03 with 3-vinyl-1-pyrazoline-5,5-d_2.

(11) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961).

(12) A dipolar transition state similar to that described by (a) T. V. Van Auken and K. L. Rinehart, Jr. [*ibid.*, **84**, 3736 (1962)] and (b) D. E. McGreer, *et al.* [*Can J. Chem.*, **43**, 1407 (1965)] is considered highly unlikely in the gas phase and would predict that **1** would be faster than **2** or **5**, and that **5** would be faster than **8** or **9**, whereas the reverse order is observed.

(13) A direct comparison is not possible since in the system under consideration a tertiary hydrogen is migrating to a primary center at 240°, whereas Setser and Rabinovitch's value comes from a secondary hydrogen migrating to a primary center, and is measured at 400°; nevertheless the agreement is very satisfactory.

therefore

$$\frac{k_{\mathrm{obsdH}}}{k_{3\mathrm{H}}} = 1 + \frac{k_{2\mathrm{H}}}{k_{3\mathrm{H}}} = 1.91$$

$$\frac{k_{\mathrm{obsdD}}}{k_{3\mathrm{D}}} = 1 + \frac{k_{2\mathrm{D}}}{k_{3\mathrm{D}}} = 1.51$$

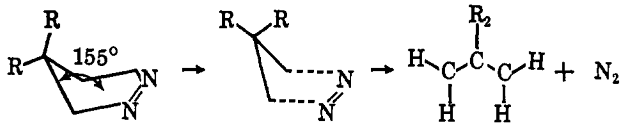
thus $k_{\mathrm{obsdH}}k_{3\mathrm{D}}/k_{\mathrm{obsdD}}k_{3\mathrm{H}} = 1.27$, and substituting the observed values for $(k_\mathrm{H}/k_\mathrm{D})_{\mathrm{obsd}}$ we find that $k_{3\mathrm{H}}/k_{3\mathrm{D}} = 0.84$, implying that the substitution of deuterium for hydrogen on C_4 increases the rate constant, k_3, by 19%, a highly improbable situation.[14] Thus we can conclude that in the pyrolysis of **3** the olefin and cyclopropane products come from a common intermediate formed after the rate-determining step. The intermediate on the basis of the kinetic observations (Table I) is a species free of nitrogen and is different from methylcyclopropane or the olefin formed therefrom.

The geometry of the transition state is revealed when we consider the rate data in Table VII. The introduction of the methyl group at the 4 position of 1-pyrazoline results in essentially no change in rate whereas the 4,4-dimethyl-1-pyrazoline is $^1/_{127}$ the rate of the reference compound. Since the ground state is not likely to be greatly affected by the introduction of the second methyl group (all of the spectroscopic properties[4] of **4** are comparable to those of 1-pyrazoline), then the decrease in rate may be attributed to steric compression in the transition state. The geometry of the pyrazolines, as inferred from nmr spectroscopy,[4,12] would appear to be similar to that of cyclopentene and have the folded arrangement **13**, with an angle between the two planes of approximately 155°. If this angle decreases as the carbon–nitrogen bonds lengthen then the geometry of the transition states approximates that of **14**, and thus the placement of a second methyl group on C_4, *cis* to the leaving nitrogen, can explain the rate depression observed. This geometry is a natural consequence of the azo link contracting from 1.25 A in the reactant and going to 1.09 A in the nitrogen molecule. This transformation is brought about by the formation of the second π bond in nitrogen and is expected to generate sp^2 hybridization at carbons C_3 and C_5. Alternatively, the slow rate of **4** would also be expected if an increase in $C_3C_4C_5$ bond angle were to occur, thus decreasing the CH_3CCH_3 angle and resulting in steric compression in the transition state.

Table VII. Relative Rate Data for Some 1-Pyrazolines at 223.0°

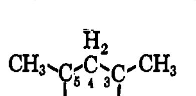
1-Pyrazolines	10^4k, sec^{-1}	Rel rate
Unsubstituted (**1**)	16.0	1.00
4-Methyl- (**3**)	15.5	0.97
4,4-Dimethyl- (**4**)	0.126[a]	0.0079

[a] Extrapolated from rates in the range 250–285°.



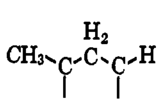
13 **14** **15**

The planar geometry for the terminal methylenes in the intermediate is further supported by the nature of the olefins arising from **6** and **7**. Their intermediates would be expected to have the geometries **16** and **17**, respectively, and thus migration of a hydrogen from C_4 in **16** to either C_3 or C_5 results in only *trans*-2-pentene being produced. Whereas the migration of a hydrogen from C_4 in **17** to C_3 results in the production of *trans*-2-pentene, the migration of a hydrogen to C_5 results in the formation of *cis*-2-pentene, as indicated in Table IV. The intermediates **16** and **17** also provide a convenient explanation for the cyclopropanes observed. If conrotation prevails[15] over that of disrotation, then the *cis* isomer **6** will give rise to *trans*-1,2-dimethylcyclopropane and the *trans* isomer **7** will give rise to *cis*-1,2-dimethylcyclopropane.



$\mathrm{CH_3\underset{H}{C}_5\overset{H_2}{C}_4\underset{H}{C}_3CH_3}$

16



$\mathrm{CH_3\underset{H}{C}\overset{H_2}{C}\underset{CH_3}{C}H}$

17

McGreer[12b] has found a similar reversal of stereochemistry during the gas phase pyrolysis of 3,5-disubstituted pyrazolines. On going to solution phase pyrolysis McGreer observed a decrease in the amount of stereochemical reversal, and in the case of 4,4-dialkyl-1-pyrazolines an increase in the rate of nitrogen evolution on increased polarity of solvent. This along with Wagner–Meerwein[16a] rearrangement of the alkyl groups led McGreer to suggest an ionic mechanism for some of the reactions in solution. Thus in solution it seems quite possible that more than one mechanism may exist,[16] or that a preference for conrotation may no longer prevail.[16b] The stereochemistry of 3,4-disubstituted pyrazolines studied by Van Auken and Rinehart[16c] present a further complexity in that for an intermediate such as the "π-cyclopropanes" (see below) two conrotatory operations to cyclopropane products are possible, each giving rise to a different stereoisomer. It is noteworthy that **4** gave rise to no olefin indicative of a Wagner–Meerwein rearrangement resulting from an ionic intermediate.

Compound **4** is worthy of one further comment in that it consistently gave rise to some methylpropene (Table III), a cleavage product, and was the only pyrazoline to do so. Cleavage has also been observed in the photolysis of **1** and is under further investigation at this time.[17]

The intermediate may be looked upon as a diradical, and the kinetic evidence is just that which one might expect for diradical formation. The nature of the products, in particular those from **6** and **7**, do not indicate the two terminal carbons to be free of one an-

---

(14) Setser and Rabinovitch[3a] have observed a mechanistic secondary isotope effect of a similar type in the pyrolysis of 1,2-dideuterio-3-methylcyclopropane and assign it a value $k_{i\mathrm{H}}/k'_{i\mathrm{H}} = 1.10 \pm 0.03$, which would imply that we could expect a 10% *decrease* in rate for k_3 on going from **3** to **12**.

(15) R. Hoffmann, Abstracts of the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper 109 K, suggests that conrotation will prevail for the "trimethylene intermediate" in its lowest singlet state.

(16) (a) D. E. McGreer, R. S. McDaniel, and M. G. Vinje, *Can. J. Chem.*, **43**, 1389 (1965); (b) C. G. Overberger, N. Weinshenker, and J. P. Anselme, *J. Am. Chem. Soc.*, **87**, 4119 (1965); (c) T. V. Van Auken and K. L. Rinehart, *ibid.*, **84**, 3736 (1962).

(17) R. Moore, unpublished results this laboratory.

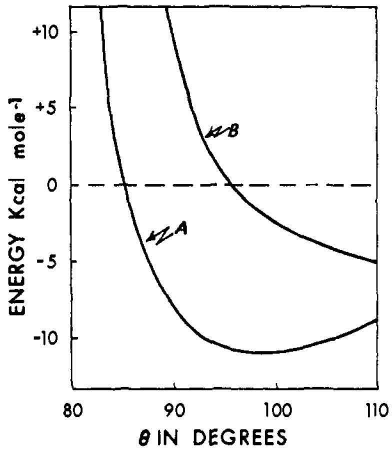


Figure 2. A plot of "π-cyclopropane" stability *vs.* θ, the angle at C_4. An arbitrary zero is taken as the trimethylene diradical wherein there is no bonding between the p orbitals in the terminal carbons. Plot A represents the results obtained using the H · · · H repulsion term of ref 21, plot B using that of ref 22.

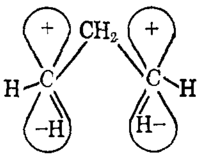
other's influence. Because of the proximity of the two sp^2 carbons it is possible that $p\pi$–$p\pi$ bonding can occur to form species **18**, which adopting spectroscopic notation would be "π_g-cyclopropane." In attempting to evaluate the possibility of this species we have assumed that the three most important terms are (a) the angle strain as evaluated by Westheimer's equation[18] where θ is the $C_3C_4C_5$ angle, (b) the π bond energy β' estimated from eq 5[19] using Slater overlap integrals,[20]

$$E = 17.5(109.5° - \theta)^2 \text{ cal mole}^{-1} \qquad (4)$$

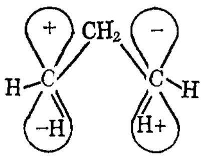
$$\beta' = \beta\frac{S'/(1 + S')}{S/(1 + S)} \qquad (5)$$

and (c) a function designed to give H···H nonbonded repulsion energies. The plot, Figure 2, shows a minimum at $\theta \simeq 100°$ for a species having a π bond between C_3 and C_5, if the H···H repulsion term used is that of Coulson and Haigh.[21] One has considerable selection of functions of this type, a "harder" function[21] being the nonbonded repulsion energies of Simmons and Williams.[22] When this function is used the minimum apparently lies above 109° 28′. The latter function for nonbonded repulsions has been highly successful in calculating conformational energy barriers and is probably the most appropriate. The calculation does, however, indicate that the interaction of the p orbitals does not allow the "diradical" to be a pair of freely acting radicals and further suggests a bonding energy of 8–12 kcal mole^{-1}. This species would then satisfy the requirements of an intermediate which must have an activation energy to be converted into cyclopropane and propylene and is capable of explaining olefinic products arising from its isomeric pyrazolines **6** and **7**. Thus geometries **16** and **17** have considerable merit.

The conversion of 1-pyrazoline into an intermediate can be treated as an electrocyclic transformation[23] and would fall into the classification of $2\sigma \rightarrow 2\pi$. Such a transformation is considered to be not allowed thermally (*e.g.*, the cyclobutane to ethylene pyrolysis) for both π bonds being symmetric. However, Hoffmann[15] has suggested from extended Hückel calculations that the potential surface of trimethylene is such that a species exists having a $C_3C_4C_5$ bond angle of roughly 125° and will be a singlet with both of its electrons in an antisymmetric orbital, *i.e.*, the "π_u-cyclopropane" (**19**). The immediate consequence of this is that conrotatory closing to cyclopropane would be preferred, in agreement with the experimental observations herein.[24] The thermal transformation to this species is allowed, and implies that the intermediate would be expected to add 1,2 to olefins. Attempts to trap the intermediate during pyrolysis with cyclohexene failed to alter the reaction course. In comparison Bartlett[25] has observed that "the evidence of rotation suggests a fully free biradical" in his studies of cycloaddition reactions forming 1,4 diradicals as intermediates. The present intermediate, from pyrazoline pyrolysis, fulfills the requirements of a "virtual diradical."[25,26] Thus the question of "when is a diradical not a diradical?" may be answered by going from a 1,4 to a 1,3 system. However, the answer may not be that simple because Simmons[27] has carried out a Pariser–Parr–Pople MO calculation on trimethylene and has found that a triplet state, as distinguished from the two singlet species **18** and **19**, is predicted to be the most stable trimethylene.



18



19

A comparison of the kinetic parameters for azoethane decomposition (E_a = 48.5 kcal mole^{-1}, ΔS^* = 12.5 eu)[28] with those of 1-pyrazoline (**1**) indicates that the activation energy is 6.1 kcal mole^{-1} lower for the later. This decrease in activation energy may be due to some 1,3 interaction in the transition state of **1** not present in the azoethane decomposition. It is not possible, as yet, to evaluate the difference in *cis* and *trans* geometries about the azo link of azoethane and thus whether steric factors are important to this difference. However, *cis–trans* relationships in alkenes (*e.g.*, *cis*-2-butene to *trans*-2-butene) give rise to values

---

[18] F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 533. This function is best in the range θ = 109 to 90°; thus the values applied here below 90° are only approximations.

[19] J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1962, p 82.

[20] K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 470.

[21] C. A. Coulson and C. W. Haigh, *Tetrahedron*, **19**, 527 (1963); T. L. Hill, *J. Chem. Phys.*, **14**, 465 (1946); **16**, 399, 938 (1948).

[22] H. E. Simmons and J. K. Williams, *J. Am. Chem. Soc.*, **86**, 3222 (1964).

[23] R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395, 2046, 2511, 4388, 4389 (1965); and H. C. Longuet-Higgins and W. E. Abramson, *ibid.*, **87**, 2045 (1965).

[24] Inasmuch as species **18** and **19** are not greatly different in energy,[15] it is possible that an equilibrium $\pi_u \rightleftarrows \pi_g$ exists that controls the amount of *cis* and *trans* products from **16** and **17**. This is consistent with **17** having a greater propensity to conrotate since the angle at the methylene group would be expected to be larger in **17** than in **16**, thus creating a preference for the π_u state.

[25] L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964), and earlier papers in the same series.

[26] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 10 (1962).

[27] H. E. Simmons, private communication.

[28] W. D. Clarke, Ph.D. Dissertation, University of Oregon, Eugene, Ore., 1959.

Table VIII. Butene Product Proportions from Pyrolysis of **2** and Methylcyclopropane

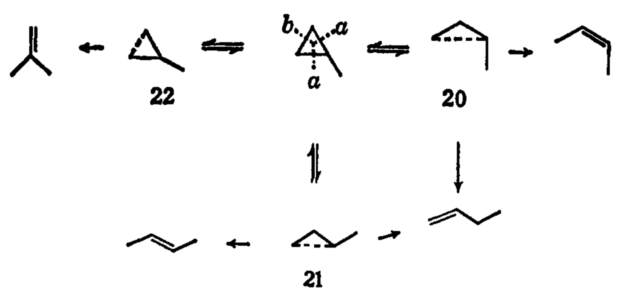
Reactant	Temp, °C	1-Butene	*cis*-2-Butene	*trans*-2-Butene	Other
2	250	1.0[a]	0.53 ± 0.05[b]	0.35 ± 0.05	 25.0
Methylcyclopropane[1a]	400	1.0	0.71	0.30	 0.18
Methylcyclopropane[1b]	469	1.0	0.63	0.28	 0.23

[a] Relative to 1-butene as a result of six runs. [b] Corrected for thermal conductivities as per ref 9.

considerably smaller than this, and thus the activation energies for pyrazoline pyrolysis may be lower because of the stability of the singlet "π_u-cyclopropane" species (**19**) being formed in the transition state.

As indicated at the beginning of this paper the pyrazoline decompositions were undertaken to help illucidate the mechanism of the cyclopropane-to-propylene isomerization process. We have shown that we produce an intermediate on the pyrolysis of 1-pyrazolines that gives rise to cyclopropanes and olefins. That this intermediate lies on the reaction profile for the conversion of cyclopropane to propylene has yet to be demonstrated. The yield of propene (10.8%) relative to cyclopropane on pyrolysis of **1** agrees well with that predicted. Benson,[29] from calculations based on the intermediacy of the trimethylene "diradical" in the isomerizations of cyclopropane and from methylene addition to ethylene, predicted that such an intermediate will partition into about 90% cyclopropane and 10% propylene in agreement with the experimental results of Rabinovitch;[30] thus the data suggest that these processes and the pyrolysis of **1** have a common intermediate. Table VIII compares the olefins produced on pyrolysis of **2** with those produced by pyrolysis of methylcyclopropane. We did not find a significant temperature dependence for product formation over a 75° temperature range, but, considering the temperature differences in the two processes, we find that the results tend to confirm the assumption of an intermediate common to both processes. The fact that 1-butene is the olefin found in greatest yield may be due to the possibility of its arising from either of the isomeric intermediates (**20** and **21**) produced, whereas the *cis*- and *trans*-2-butenes can each arise from only one intermediate. The yield of *cis*-2-butene also suggests that the $C_3C_4C_5$ bond angle is large since a small angle would increase the $H \cdots CH_3$ repulsion and make **20** less probable than **21**.

The products of pyrolysis of 1,1-dimethylcyclopropane at 447° have been observed by Flowers and Frey to consist of 2-methyl-2-butene, 3-methyl-1-butene, and 2-methyl-1-butene in the ratio 1.0:1.06:0.018.[31] The pyrolysis of **5** at 202° gives the same olefins in the ratio 1.0:0.85:trace, indicative of a common intermediate in both reactions. The products of pyrolysis of other cyclopropanes indicate a quantitative similarity with those obtained by pyrazoline pyrolysis (Table III) and supports the geometry of the intermediate suggested as being a reasonable species in such reactions as cyclopropane and pyrazoline pyrolysis and for the addition[15] of methylene species to olefins.



21

Acknowledgment. The authors are grateful to the Petroleum Research Fund of the American Chemical Society (Grant 1770-A4) and to the National Research Council of Canada for support of this work.

(29) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(30) B. S. Rabinovitch, E. Tschuikow-Roux, and E. W. Schlag, *J. Am. Chem. Soc.*, **81**, 1081 (1959).

(31) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3953 (1959).