The Synthesis and Physical Properties of Some 1- and 2-Pyrazolines[1]

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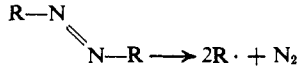
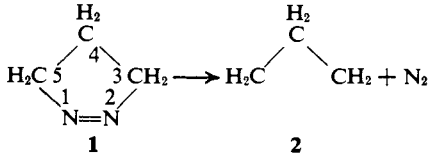
Abstract: The synthesis and spectra of 1-pyrazoline and 3-methyl-, 4-methyl-, 4,4-dimethyl-, 3,3-dimethyl-, 3,3,5-trimethyl-, and 3,3,5,5-tetramethyl-1-pyrazoline along with their pyrazolidine precursors are discussed. The synthesis, spectra, and assignment of structure to *cis*- and *trans*-3,5-dimethyl-1-pyrazoline are also presented. The resolution of *trans*-3,5-dimethyl-1-pyrazoline is reported.

The mechanism of the thermal isomerization of cyclopropane to propylene has stimulated the production of numerous papers since its first kinetic study[4] in 1922. The elegant work of Rabinovitch[5] provides an excellent discussion of mechanistic developments in this line. A frequently suspected intermediate in this reaction is a 1,3 diradical. The evidence for its existence, however, is not compelling, and hydrogen migration concerted with ring opening has been proposed to account for the kinetic isotope effects of deuterated cyclopropanes.[6] The existence of an activated complex having the geminal hydrogens of one of the methylene groups in the same plane as the carbon atoms has also been proposed to account for structural isomerization.[7] More recently DeMore and Benson[8] have vigorously supported the 1,3-diradical species as an intermediate.

We have taken the approach, that has been so fruitful to mechanistic studies in the past, of attempting to produce the intermediate from an alternate source. In this instance the evidence for the formation of two radicals by the thermal decomposition of azoalkanes, particularly the more symmetrical species,[9] suggested



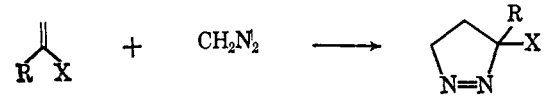
that a study of 1-pyrazoline (**1**) could potentially be of value in forming the 1,3-diradical **2**. To this end we have undertaken the synthesis of **1** and other alkyl-



1 **2**

pyrazolines. This, the first paper, covers the synthesis and structure proof of these molecules; the second paper[10] presents the kinetics and mechanism of their thermal decomposition and the relationship of the products from these processes to the cyclopropane pyrolysis products.

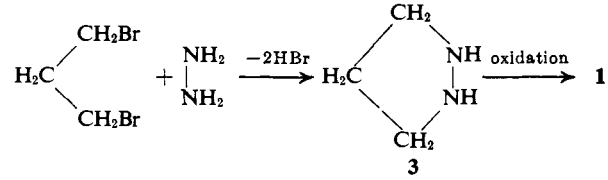
The Synthesis of 1-Pyrazolines. 1-Pyrazolines are generally prepared by the addition of diazomethane to olefin double bonds activated by electron-withdrawing groups. This method has been successfully employed



X=CO_2R, COR, CN, NO_2, and C_6H_5—

by McGreer,[11a] *et al.*, in the synthesis of a number of interesting 1-pyrazolines. The slowness of this reaction with alkenes[11b] is such that it cannot profitably be used for the synthesis of **1** nor other alkylated pyrazolines.

The synthesis of pyrazolidine (**3**) from 1,3-dibromopropane and hydrazine has been reported[12] and offers a route analogous to that of the synthesis of azoethane. However it is evident from previously reported[11a]



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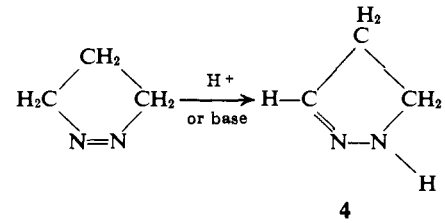
pyrazolines that 1-pyrazolines tautomerize readily to 2-pyrazolines (**4**) both in acid or base; thus the oxidation and work-up should be rapid and as near neutrality



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as possible. A procedure using molecular oxygen, similar to the diimide preparation, was investigated.

(1) Part of this work was reported as a preliminary communication: R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3023 (1965).
(2) National Research Council of Canada Studentship Holder, 1964–1965.
(3) University of Alberta Postdoctoral Fellow, 1963–1964.
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(7) F. T. Smith, *J. Chem. Phys.*, **29**, 235 (1958).
(8) W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 255 (1964).
(9) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961); **85**, 14 (1963). More recently Seltzer has reported a case of one bond cleavage in an unsymmetrical azo compound; see S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965).
(10) R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966).
(11) (a) D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. Wong, *Can. J. Chem.*, **43**, 1407 (1965), and previous papers in that series; (b) L. Ali, unpublished results from this laboratory.
(12) E. L. Buhle, A. M. Moore, and F. Y. Wiselogle, *J. Am. Chem. Soc.*, **65**, 29 (1943).

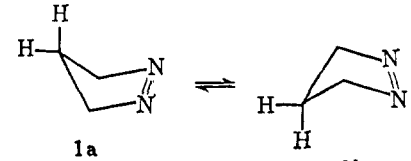
Table I. The Yields, Physical Properties, and Elemental Analyses for the 1-Pyrazolines

	Compound	% yield[a] (HgO method)	Bp, °C (mm)	$n^{25}D$	Infrared (CCl_4) $\nu_{N=N}$, cm^{-1}	Ultraviolet (MeOH) λ_{max}, mμ (ε)	Elemental analysis, % Calcd C	Calcd H	Calcd N	Found C	Found H	Found N
1	1-Pyrazoline	60	61–62 (40)	1.4360	1545	315 (446)	51.40	8.63	39.97	51.73	8.85	39.91
2	3-Methyl-1-pyrazoline	75	53–54 (40)	1.4335	1540	319 (380)	57.11	9.57	33.32	56.80	9.22	33.54
3	4-Methyl-1-pyrazoline	50	58–60 (40)	1.4355	1545	318 (310)	57.11	9.57	33.32	56.90	9.76	33.40
4	4,4-Dimethyl-1-pyrazoline	60	Mp 40–42°	...	1543	323 (325)	61.19	10.28	28.53	61.04	10.37	28.71
5	3,3-Dimethyl-1-pyrazoline	60	51–52 (40)	1.4305	1550	321 (284)	61.19	10.28	28.53	61.30	10.41	28.43
6	*cis*-3,5-Dimethyl-1-pyrazoline[b]	70	60–61 (40)	1.4285	1545	323 (300)	61.19	10.28	28.53	61.40	10.08	28.60
7	*trans*-3,5-Dimethyl-1-pyrazoline[c]	70	60–61 (40)	1.4347	1545	323 (300)	61.19	10.28	28.53	61.13	10.16	28.51
8	3,3,5-Trimethyl-1-pyrazoline	80	64–65 (40)	1.4300	1545	325 (371)	64.24	10.78	24.98	64.12	10.52	25.15
9	3,3,5,5-Tetramethyl-1-pyrazoline	70	Mp 28–30°	...	1550	324 (160)	66.62	11.18	22.20	66.53	11.29	22.12

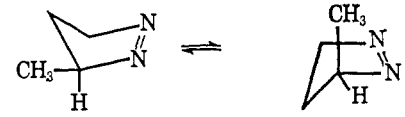
[a] HgO method. [b] Contained about 2% of the *trans* isomer as determined by nmr (HR-100). [c] Contained about 5% of the *cis* isomer as determined by nmr (HR-100).

Using aqueous methanol as a solvent, and cupric acetate as a catalyst, pyrazoline (**1**) was obtained in a 70% yield. The procedure, however, was slow and the use of mercuric oxide or silver oxide in pentane, with a suspension of magnesium sulfate, gave good yields in a shorter period of time and has proven to be the method of choice. Table I presents the physical constants for the 1-pyrazolines prepared from the corresponding pyrazolidines.

Spectral Properties of the 1-Pyrazolines. The nmr spectra of the pyrazolines listed in Table I are well resolved and informative. As has been observed by McGreer,[11a] *et al.*, the nmr spectra have distinct conformational implications. Spectra for the entries 1, 4, 5, 7, and 9 in Table I indicate that the protons or methyls at C_4 are equivalent. Spectra for entries 2, 6, and 8 indicate nonequivalence, resulting in AB spectra, for the methylene hydrogens at C_4. Pitzer, *et al.*,[13] have shown that the folding of the C_4 center in cyclopentenes out of the plane of the other atoms in the ring partially removes the eclipsed interactions in the planar structure causing very small angle strain. The detailed parameters of the cyclopentene ring, from microwave spectroscopy,[14] indicate that the angle between $C_3C_4C_5$ and $C_1C_2C_3C_5$ is 22° 18′. Models indicate that the 1-pyrazoline ring would be expected to have even a greater puckering at C_4 by decreasing the interatomic distance on going from HC=CH (1.35 A) to −N=N− (1.25 A). McGreer,[15] *et al.*, have calculated an angle of about 25° between the $C_3C_4C_5$ and C_3C_5NN planes in the 1-pyrazoline ring on the basis of coupling constants between the protons at C_4 and at C_3 or C_5. Their arguments are readily extended to the 1-pyrazolines we have studied. Thus to explain the equivalence or nonequivalence of the C_4 protons, we consider the equilibrium, **1a** ⇄ **1b** and **5a** ⇄ **5b**. Preference for the form **5a** in the latter equilibrium (due to the 1,3 axial CH_3–H interaction) causes the C_4 protons to be nonequivalent, whereas equal population and rapid interconversion of **1a** and **1b** renders the C_4 protons equivalent.[16] The importance of the conformational

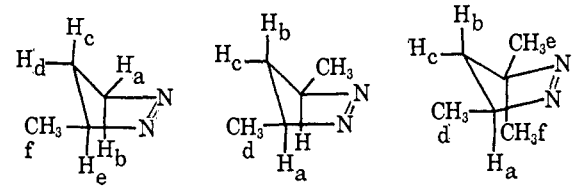


1a **1b**

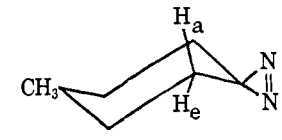


5a **5b**

equilibrium, in those compounds having equivalent methylene protons at C_4, is reflected in the chemical-shift positions in that they take a median position between the chemical shifts observed when the C_4 protons are nonequivalent. The large difference in chemical-shift positions between the nonequivalent protons on C_4 (0.78 ppm in **5**, 1.60 in **6**, and 0.92 in **7**) is indicative of secondary anisotropic magnetic fields, possibly due to the π electrons of the azo group. Similar anisotropic effects due to −N=N− have been observed by Uebel and Martin[17] in the cyclohexane derivatives containing a diazirine ring (**8**) wherein the proton H_e was observed to resonate at 1.57 ppm to



5 **6** **7**



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(13) C. W. Beckett, M. K. Freeman, and K. S. Pitzer, *ibid.*, 70, 2447 (1948).

(14) G. W. Rathjens, *J. Chem. Phys.*, 36, 2401 (1962).

(15) D. E. McGreer, N. W. K. Chiu, and M. G. Vinje, *Can. J. Chem.*, 43, 1398 (1965).

(16) Attempts to gain further evidence by low-temperature nmr have not been successful because of solubility problems; even so, the small barrier[14] in cyclopentene, 0.56 kcal $mole^{-1}$, would indicate that a sufficiently low temperature might not be accessible.

(17) J. J. Uebel and J. C. Martin, *J. Am. Chem. Soc.*, 86, 4618 (1964).

Table II. Coupling Constants and Chemical Shifts for Pyrazolines Displaying AB Spectra at C_4

Compd	Coupling constants, cps	Chemical shifts, τ
5	$\|J_{ab}\| = 16.8$	$H_a = 5.57$
	$J_{ac} = 9.6$; $J_{bc} = 8.0$	$H_b = 5.90$
	$J_{ad} = 5.0$; $J_{bd} = 9.3$	$H_c = 9.01$
	$J_{ae} = 2.3$; $J_{be} = 2.0$	$H_d = 8.27$
	$J_{de} = 8.5$; $\|J_{cd}\| = 12.3$	$H_e = 5.71$
	$J_{ef} = 6.9$; $J_{ce} = 7.5$	$H_f = 8.62$
6	$J_{ab} = 9.3$	$H_a = 5.80$; $H_c = 8.92$
	$J_{ac} = 8.2$	$H_b = 9.52$; $H_d = 8.46$
	$J_{ad} = 7.0$	
	$\|J_{bc}\| = 12.5$	
7	$J_{ab} = 8.5$	$H_a = 5.60$; $H_d = 8.57$
	$J_{ac} = 8.0$	$H_b = 9.38$; $H_e = 8.60$
	$J_{bc} = 12.5$	$H_c = 8.22$; $H_f = 8.87$

Table III. Physical Properties of Pyrazolidines

Compound	Method of prepn[a]	% yield	Bp, °C (40 mm)	$n^{25}D$
Pyrazolidine[12]	A	70	66, 138 (700)	1.4560
	B	30		
3-Methylpyrazolidine	A	75	65–67	1.4557
4-Methylpyrazolidine	A	50	69–70	1.4583
	B	7		
4,4-Dimethylpyrazolidine	A	65	66–67	1.4530
3,3-Dimethylpyrazolidine	A	60	66–67	1.4485
cis-3,5-Dimethylpyrazolidine	B	27	69–70	1.4510
trans-3,5-Dimethylpyrazolidine	B	50	69–70	1.4580
3,3,5-Trimethylpyrazolidine	C	40	70–71	1.4445
3,3,5,5-Tetramethylpyrazolidine[b]	B	30	Mp 26–27°	...

[a] A = catalytic reduction; B = synthesis from 1,3-dibromo compound; C = chemical reduction. [b] Bp 74–76° (40 mm) separated by preparative gas chromatography from impurities.

higher field than H_a. Table II gives the coupling constants of the pyrazolines **5**, **6**, and **7**, which are consistent with the puckered pyrazoline ring proposed by McGreer.[15]

The infrared spectra of the 1-pyrazolines all displayed the N=N stretching frequency at 1545 ± 5 cm^{-1}, at slightly lower frequency than that observed for *trans*-azoalkanes.[18] The ultraviolet spectra show the typical azoalkane n → π* absorption at 320 ± 5 mμ,[19] considerably lower than that observed for the six-membered ring homolog at 375 mμ.[20]

The Synthesis of the Pyrazolidines. As each of the 1-pyrazolines has been prepared from the corresponding pyrazolidine, it was necessary to work out synthetic methods for the precursors. The three principal methods were (a) the reaction of hydrazine with a 1,3-dihalide, (b) the reduction by sodium in alcohol, and (c) hydrogenation of the corresponding 2-pyrazoline over a platinum catalyst. The pyrazolidines prepared by the latter method failed to give satisfactory analysis, and their nmr spectra indicated that some hydrogenolysis of the N–N linkage to the corresponding diamine had occurred to the extent of 10–15%, but they were successfully employed in the synthesis of 1-pyrazolines. Table III lists the properties and yields of the pyrazolidines prepared by these procedures.

The Assignment of Configuration of *cis*- and *trans*-3,5-Dimethyl-1-pyrazoline. The reaction of *meso*- and *dl*-2,4-dibromopentane with hydrazine yielded isomeric 3,5-dimethylpyrazolidines. If the cyclization proceeds by two inversions, then *cis*- and *trans*-3,5-dimethylpyrazolidine, respectively, would be produced. Because of the unusual nature of the products upon thermal decomposition,[21] the resolution of *trans*-3,5-dimethylpyrazolidine was undertaken. This was accomplished by condensation of the isomer derived from the *dl* dibromide with hydroxymethylenecamphor. The product upon recrystallization was oxidatively converted to the same 3,5-dimethyl-1-pyrazoline as produced by mercuric oxide oxidation. This product, obtained in low yield, was purified by preparative gas chromatography and had an $[\alpha]^{25}_{450}$ +550°; the mother liquor yielded the enantiomer by a similar work-up.

Experimental Section

All melting points and boiling points are uncorrected. The infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer. The nuclear magnetic resonance spectra were measured using a Varian A-60 and a HR-100 spectrophotometer, using tetramethylsilane as an internal standard, and unless otherwise noted were run as 20% solutions in carbon tetrachloride. The optical rotations were measured with a Rudolph ORD spectropolarimeter and preparative gas chromatography was carried out on a Wilkens Aerograph Autoprep Model A-700 using a 20-ft Ucon-insol, on a Diatoport or Fluoropak support. Micronanalysis were performed by Daessle Organic Microanalysis, Montreal, and by the microanalytical laboratory of the University of Alberta.

4-Methyl-2-pyrazoline. A solution of 70 g of freshly distilled methacrolein in 50 ml of ether was added to a well-stirred suspension of 70 g of hydrazine hydrate in 150 ml of ether cooled in a salt–ice bath. The solution was extracted continuously with ether for 24 hr, and the ether layer was dried over anhydrous sodium sulfate. After the ether had been removed the residue was distilled through a 10-in vacuum-jacketed Vigreux column. The distillate weighed 25 g (30%), bp 67–69° (40 mm), $n^{25}D$ 1.4743. The nmr spectrum consisted of a broad NH singlet at τ 3.98, CH_3 doublet at τ 8.93, CH multiplet at τ 6.7, $-CH_2-$ at τ 7.0, and CH singlet at τ 3.30. The infrared spectrum displayed NH absorption at 3310 cm^{-1} and C=N at 1585 cm^{-1}, λ_{max} 230 mμ (ε 3950 in methanol).

Anal. Calcd for $C_4H_8N_2$: C, 57.11; H, 9.57; N, 33.32. Found: C, 57.23; H, 9.67; N, 33.56.

4,4-Dimethyl-2-pyrazoline. A solution of 3-hydroxy-2,2-dimethylpropionaldehyde[22] (102 g, 1 mole) in 50 ml of pyridine was added, in portions, with stirring to a solution of *p*-toluenesulfonyl chloride (200 g, 1.1 moles) dissolved in 100 ml of pyridine. The temperature was not allowed to exceed 70°. The resulting solid

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(19) C. N. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworths and Co., Ltd., London, 1961, p 347.
(20) R. Moore, unpublished results.
(21) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3768 (1965).
(22) R. Kapp, F. D. Pickel, and L. T. Rosenberg, U. S. Patent 2,434,246; *Chem. Abstr.*, **42**, 2271 (1948.)

mass was treated with water to dissolve the pyridine hydrochloride, and the lower viscous layer of the *p*-toluenesulfonate was washed twice with dilute hydrochloric acid and once with water to remove the residual pyridine. The crude ester was then added with cooling to a hydrazine hydrate (50 g, 1 mole) solution in 100 ml of ice-water. After stirring for 1 hr at room temperature, potassium hydroxide pellets (56 g, 1 mole) were added, with cooling, in small portions. The resulting viscous mass was dissolved in a small volume of water and subjected to continuous extraction with ether for 24 hr. The work-up was the same as in the previous example, bp 64–65° (40 mm), $n^{25}D$ 1.4590, 29 g (30% from the aldehyde). The nmr spectrum displayed a broad NH singlet at τ 4.80, vinyl CH at τ 3.45, $-CH_2-$ at τ 6.95, and CH_3 signal at τ 8.93 of intensities 1:1:2:6. The infrared spectrum displayed NH absorption at 3350 cm^{-1} and C=N at 1610 cm^{-1}; λ_{max} 228 mμ (ϵ 4250 in methanol). The N-phenylthiourea derivative[23] was recrystallized twice from ethanol, mp 140–142°.

Anal. Calcd for $C_{12}H_{15}N_3S$: C, 61.72; H, 6.48; N, 18.01. Found: C, 61.54; H, 6.47; N, 17.70.

3-Methylpyrazolidine. The procedure used for the reduction of 2-pyrazoline to pyrazolidine is illustrated here. A solution of 20 g of 5-methyl-2-pyrazoline[24] dissolved in 50 ml of methanol was reduced on a Parr hydrogenation apparatus, at room temperature, by using 1 g of platinum dioxide. The reduction was slow, 10 hr, and upon completion the filtrate was drained into a flask containing a small amount of ethylenediaminetetraacetic acid to minimize oxidation. The methanol was distilled off and the product was isolated by vacuum distillation, bp 65–67° (40 mm), $n^{25}D$ 1.4557.

Anal. Calcd for $C_4H_{10}N_2$: C, 55.77; H, 11.70; N, 32.53. Found: C, 55.50; H, 11.59; N, 32.42.

The pyrazolidines were found to be air sensitive and the above technique often leads to 10–20% hydrogenolysis of the N–N bond as indicated by nmr and high hydrogen analysis.

4-Methylpyrazolidine. This compound was prepared in 50% yield by the catalytic reduction of 4-methyl-2-pyrazoline, and its properties are indicated in Table III. Owing to hydrogenolysis the sample was always contaminated with 10–15% diamine (nmr). This could be successfully used in the synthesis of 4-methyl-1-pyrazoline.

4,4-Dimethylpyrazolidine. This compound was prepared in 65% yield but, as above, always had some diamine which prevented satisfactory analysis. It, however, gave good yields on oxidation to the corresponding pyrazoline (Tables I and III).

***cis*-3,5-Dimethylpyrazolidine (6).** To a well-stirred solution of 95% hydrazine (24 g, 0.75 mole) in 100 ml of 98% ethanol was added *meso*-2,3-dibromopentane[25] (25 g, 0.25 mole) in small portions. After 3 hr at room temperature the solution was cooled and the hydrazine hydrobromide was removed by filtration. The filtrate was then placed on a layer of KOH pellets for 2 hr, whereupon potassium bromide was precipitated. All the solids were removed by filtration, a small amount of EDTA was added, and the ethanol was removed by fractional distillation. Vacuum distillation of the residue yielded the product, bp 69–70° (40 mm), $n^{25}D$ 1.4510, 8 g (37%). The diphenylthiourea was prepared and upon recrystallization from ethanol gave mp 141–142°.

Anal. Calcd for $C_{19}H_{22}N_4S_2$: C, 61.58; H, 5.98; N, 15.12. Found: C, 61.70; H, 6.26; N, 14.78.

The *cis* isomer was also prepared from 3,5-dimethyl-2-pyrazoline[26] by catalytic reduction (see above) in a 50% yield.

***trans*-3,5-Dimethylpyrazolidine (7).** The same procedure used for the *cis* isomer was used except that *dl*-2,4-dibromopentane[25] was the starting dihalide. The product was isolated in 50% yield, bp 69–70° (40 mm), $n^{25}D$ 1.4580 (see below for derivative and resolution).

3,3,5,5-Tetramethylpyrazolidine. Small portions of 2,4-dibromo-2,4-dimethylpentane (42 g, 0.25 mole) were added to a solution of 95% hydrazine (24 g, 0.75 mole) in 100 ml of 98% ethanol cooled to 0°. After addition the hydrazine hydrobromide was removed by filtration and the reaction mixture was allowed to come to room temperature. Of the several work-ups tried the most successful purification resulted from preparative gc using a 20-ft Ucon-insol on Fluoropak column. The product isolated in 30% yield by gc, mp 26–27°, was found to be sensitive to air and was converted to its N-phenylthiourea derivative, mp 130–131° (from ethanol).

Anal. Calcd for $C_{14}H_{21}N_3S$: C, 63.83; H, 8.03; N, 15.95. Found: C, 63.76; H, 8.19; N, 16.03.

3,3,5-Trimethylpyrazolidine. To a solution of 3,3,5-trimethyl-2-pyrazoline[27] (40 g, 0.4 mole), in 1 l. of 1-butanol, was added, in small portions, sodium (70 g, 3 g-atoms). The resulting product was washed with a salt water solution and the organic layer was subjected to fractional distillation. The 3,3,5-trimethylpyrazolidine (20 g, 40%) distilled at 70° (40 mm), $n^{25}D$ 1.4445 (lit.[28] $n^{20}D$ 1.4441).

Resolution of *trans*-3,5-Dimethyl-1-pyrazoline (7). A solution of *trans*-3,5-dimethylpyrazolidine (10 g, 0.1 mole) in 50% acetic acid (20 ml) was added to hydroxymethylene-*d*-camphor[29] (36 g, 0.20 mole) dissolved in a small amount of methanol. The resulting yellow solution was warmed on a water bath for 10 min and then neutralized with 40% sodium hydroxide. An orange-yellow oil separated out and very quickly crystallized when cooled to 0°. The solid was separated from the alkaline layer and washed twice with water. The wet crystals were dissolved in 30 ml of warm methanol and water was added until the cloudiness persisted on warming. Cooling the solution overnight produced 10 g of crystals, mp 190–195°, $[\alpha]^{25}D$ +310° (c 2 × 10^{-2}, methanol). Two further recrystallizations raised the melting point to 231–232°, $[\alpha]^{25}D$ +320°.

Anal. Calcd for $C_{27}H_{40}N_2O_2$: C, 76.87; H, 9.50; N, 6.60. Found: C, 76.61; H, 9.32; N, 6.66.

The condensation product (3 g) was dissolved in 15 ml of methanol, and bromine (0.72 ml) was added dropwise. After the addition was complete the methanol was removed under reduced pressure, and warm water was added to the residual mass. The mixture was then extracted five times with benzene to remove the hydroxymethylene-*d*-camphor derivatives. The aqueous solution was then concentrated and neutralized with sodium hydroxide. Ether extraction followed by silver oxide oxidation (see below) resulted in the formation of *trans*-3,5-dimethyl-1-pyrazoline which was isolated by preparative gc (5% yield). The product showed a positive Cotton curve, with a peak at 340 mμ; ORD (c 1 × 10^{-3}, methanol, 25°) $[\alpha]_{600}$ +250°, $[\alpha]_{450}$ +550°, $[\alpha]_{400}$ + 780°. The infrared spectrum was identical with that of a sample of 3,5-dimethyl-1-pyrazoline obtained from the reaction of *dl*-2,4-dibromopentane with hydrazine, thus requiring this to be the *trans* isomer.[30]

The mother liquor, from which the first crop of condensation product was isolated, was concentrated and yielded 6 g of an amorphous material, mp 88–90°, $[\alpha]^{25}D$ +270° (c 2 × 10^{-2}, methanol). This was converted by the same procedure to *trans*-3,5-dimethyl-1-pyrazoline, preparative gc, which displayed a negative Cotton curve; ORD (c 6 × 10^{-4}, methanol, 25°) $[\alpha]_{600}$ −135°, $[\alpha]_{450}$ −300°, $[\alpha]_{400}$ −500°.

Observations below 340 mμ were complicated by the light absorption and accompanying photolysis generating bubbles in the solution.

Oxidation of Pyrazolidines to 1-Pyrazolines. The three procedures described below were used to oxidize the pyrazolidines to the 1-pyrazolines. Yields, physical properties, and analytical data are reported in Table I.

(a) Oxidation by Mercuric Oxide. The pyrazolidine to be oxidized (0.05 mole) was dissolved in 10 ml of pentane and the solution was added slowly to a well-stirred slurry of red mercuric oxide (22 g, 0.1 mole) and anhydrous sodium sulfate in 100 ml of pentane cooled to 0°. After the addition was complete the mixture was allowed to come to room temperature with continuous stirring. The reaction could be followed by the growth of the 1-pyrazoline peak by gc on a Ucon-insol column. When the oxidation was complete (1 to 3 hr), the pentane solution was decanted and the solid was triturated with pentane. The extracts were combined and the product was isolated by fractional distillation.

(b) Oxidation by Silver Oxide. This procedure is similar to that above, except silver oxide and methanol were used. The

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(30) Additional support for this assignment comes from the Auwers-Sitka rule as modified by Allinger[31] which states that the conformationally less stable form (here, the *trans*) will have higher physical constants. The index of refraction for the *trans*-3,5-dimethylpyrazolidine and *trans*-3,5-dimethyl-1-pyrazoline are higher than those of their respective *cis* isomers. See Tables I and III.

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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.

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

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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 ± 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-

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