Thermolysis of 3,3,5,5-Tetramethyl-4-methylene-1-pyrazoline and the Thermal Isomerization of Some Alkylidenecyclopropanes

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The thermolysis of 3,3,5,5-tetramethyl-4-methylene-1-pyrazoline (**1**) proceeds at 1/63 the rate of 4-methylene-1-pyrazoline. The activation parameters, $\log(k/s^{-1}) = (15.53 \pm 0.3) - (40.7 \pm 0.4)/\theta$ where $\theta = 2.303\,RT$ in kcal mol^{-1}, suggest that **1** is undergoing thermolysis by a mechanism different from that for 4-methylene-1-pyrazoline. The 2,2,3,3-tetramethylmethylenecyclopropane (**5**) produced rapidly isomerizes under the reaction conditions to 2,2-dimethylisopropylidenecyclopropane (**4**). The four opposed methyl groups of **5** have created sufficient ground state destabilization as to cause its isomerization to be 147 times faster than the conversion of 2,2-dimethylmethylenecyclopropane to isopropylidenecyclopropane.

The products are considered in terms of two possible intermediates, one wherein an allylic diazenyl diradical is considered and the second wherein a Chesick type of intermediate is invoked. For the latter it is demonstrated that substituents on the orthogonal radical center can affect the rotational propensities of methylene *vs.* isopropylidene of the allylic system.

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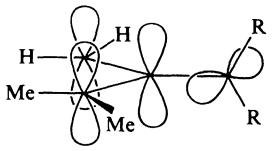
La thermolyse de la tétraméthyl-3,3,5,5-méthylène-4-pyrazoline-1 (**1**) s'effectue avec une vitesse égale à 1/63 de la vitesse de décomposition de la méthylène-4-pyrazoline-1. Les paramètres d'activation, $\log(k/s^{-1}) = (15.53 \pm 0.3) - (40.7 \pm 0.4)/\theta$ ou $\theta = 2.303\,RT$ en kcal mol^{-1}, suggèrent que **1** subit la thermolyse selon un mécanisme différent de celui de la méthylène-4-pyrazoline-1. Le tétraméthyl-2,2,3,3-méthylènecyclopropane (**5**) produit, s'isomérise rapidement, dans les conditions de la réaction, pour donner le diméthyl-2,2-isopropylidènecyclopropane (**4**). Les quatre groupes méthyle opposés de (**5**) créent une déstabilisation de l'état fondamental suffisante pour que son isomérisation soit 147 fois plus rapide que la conversion du diméthyl-2,2-méthylènecyclopropane en isopropylidènecyclopropane.

On considère les produits en faisant intervenir deux intermédiaires possibles, l'un dans lequel un diradical allylique–diazényl est considéré et le second dans lequel un intermédiaire du type Chesick est invoqué. Pour ce dernier, il est démontré que les substituents sur le centre radicalaire orthogonal peuvent affecter la tendance à la rotation du groupe méthylène par rapport au groupe isopropylidène du système allylique.

Introduction

As a consequence of our work on the thermolysis of 4-alkylidene-1-pyrazolines (1) we have carried out an investigation of the gas phase thermolysis of 3,3,5,5-tetramethyl-4-methylene-1-pyrazoline (**1**). This structure has the advantage that the tautomerism, which plagued our previous studies, is no longer possible. Our principal objectives in studying **1** were to compare the competition between the isopropylidene group and the methylene group, of the presumed intermediate **2***a*, with the same competition observed in **2***b*, the implied intermediate in the thermolysis of 4-isopropylidene-1-pyrazoline (1), and to examine the thermolysis kinetics of a substituted 4-alkylidene-1-pyrazoline.



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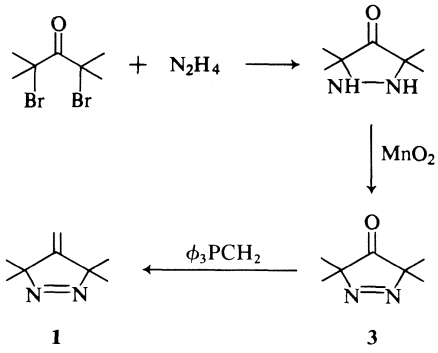
a R = Me

b R = H

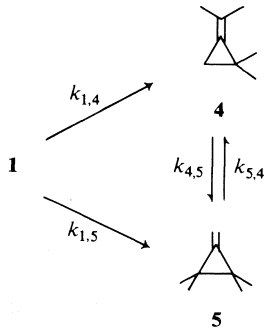
The synthesis of **1** has been reported and we followed Mock's (2) procedure for the transformation of **3** to **1**. We prepared **3** by the oxidation of the corresponding tetramethyl-4-pyrazolidone which was readily prepared by the reaction of hydrazine and α,α′-dibromodiisopropylketone.



Much to our surprise we found the thermolysis of **1** to be somewhat slower than 4-methylene-1-pyrazoline and our initial investigation suggested that only one product, 2,2-dimethylisopropylidenecyclopropane (**4**) was produced. However, careful examination of the gas chromatograph of the products on low conversion revealed that 2,2,3,3-tetramethylmethylenecyclopropane (**5**) was present and that it was rapidly isomerizing under the reaction conditions. It became necessary to study the interconversion and thermodynamic stability of **4** and **5** and thus we report herein on the mechanism of the thermolysis of **1** and the isomerization of **4** and **5**.

Results

The thermolysis of **1** at 400 Torr was carried out in sealed ampoules. After heating in a constant temperature bath the ampoules were reattached to the vacuum line and the product was transferred to a sample tube, toluene added, and the concentrations of **1**, **4**, and **5** measured by analytical gas chromatography (g.c.). Table 1



gives a sample rate at 165.2° along with the proportions of **4** and **5** present. The rate constants and activation parameters for the thermolysis of **1** are given in Table 2.

TABLE 1. Thermolysis of **1** in the gas phase at 180.17 ± 0.02°

Time (min)	**1** (%)	**5**:**4**	$10^5 k$ (s^{-1})
15.0	94.0±0.5[a]	0.7018±0.0011[a]	
30.0	87.7±0.3	0.4910±0.0010	
45.0	82.0±0.6	0.3616±0.0009	7.97 ± 0.08
60.0	75.9±0.7	0.2773±0.0009	
90.0	66.6±0.8	0.1803±0.0007	
120.0	57.6±0.7	0.1244±0.0009	
150.0	49.7±0.6	0.0921±0.0007	
180.0	42.4±0.3	0.0700±0.0005	

[a]The error listed is the standard deviation of nine analyses, triplicate analyses on three tubes at each time.

A pure sample of **5** was obtained by the preparative g.c. separation of a 57:43 mixture of **5**:**4**. This mixture was obtained from the direct photolysis, at 0°, of **1** in pentane using Pyrex-filtered radiation from a 450 W Hanovia high pressure lamp. No attempt was made to carry out a photochemical study but the length of time required for 98% conversion, 72 h, and the constancy of the 57:43 ratio throughout the reaction was ascertained from following the reaction by g.c. analysis.

At temperatures high enough so that equilibrium could be attained in a reasonable time, either **4** or **5** gave the same equilibrium mixture of starting material and product. The amount

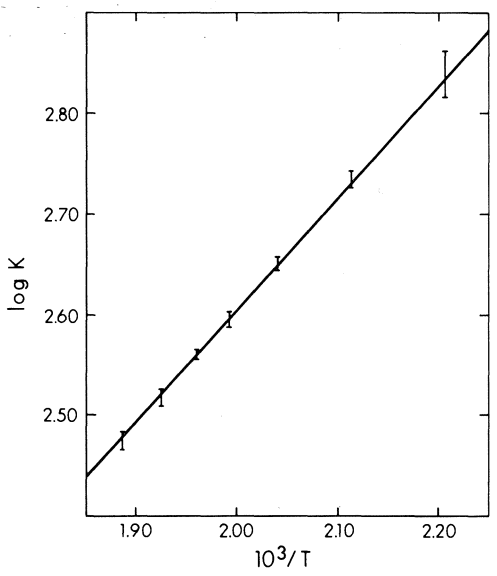


FIG. 1. Temperature dependence of the 2,2,3,3-tetramethylmethylenecyclopropane and 2,2-dimethylisopropylidenecyclopropane equilibrium constant with the best fit line from a least-squares calculation.

TABLE 2. Rate constants and activation parameters for the thermolysis of **1**

Temperature (°C)	$10^5 k_s$ (s^{-1})	Activation parameters
165.15±0.02	1.64±0.04	E_a = 40.7 ± 0.4 kcal mol^{-1}
		log A = 15.53
180.17±0.02	7.97±0.08	
		$\Delta H^{\ddagger}$ = 39.8 ± 0.4 kcal mol^{-1}
200.11±0.03	52.1±0.3	$\Delta S_{150}{}^{\ddagger}$ = +9.8 ± 0.9 e.u.

TABLE 3. Equilibrium data for **4** ⇄ **5** at various temperatures (K = [**4**]/[**5**])

Temperature (°C)	Reaction time (h)	%**5** at equilibrium	K^a
180.15	144	0.16±0.02	653±33[b]
200.11	24	0.20±0.01	512±10
217.10	16	0.24±0.01	421±8
228.85	10	0.27±0.01	371±7
237.30	10	0.29±0.01	343±4
246.35	6	0.32±0.01	311±8
258.60	6	0.35±0.01	281±6

[a]Calculated directly from integration data using a Perkin-Elmer 900 g.c. equipped with a Hewlett Packard 3370A Electronic Integrator. The relative sensitivities of 5 and 4 to the flame ionization detector was 1.00 ± 0.01.
[b]Error listed is the standard deviation of nine analyses, triplicate analyses on each of three samples.

TABLE 4. First-order rate constants for the rearrangement of **5** to **4** ($k_{5,4}$)

Temperature (°C)	$10^5 (k_{5,4}+k_{4,5})$ (s^{-1})	Activation parameters
145.28±0.03	1.80±0.02	E_a = 36.4 ± 0.03 kcal mol^{-1}
		log A = 14.27
155.22±0.02	4.91±0.05	
		$\Delta H^{\ddagger}$ = 35.6 ± 0.3 kcal mol^{-1}
165.28±0.02	13.3±0.1	$\Delta S_{150}{}^{\ddagger}$ = +4.0 ± 0.9 e.u.

of **5** at equilibrium was so small that the samples had to be handled with care to prevent any preferential loss of the more volatile **5**. A break-seal containing a 10 μl sample of **4**, or **5**, was carefully degassed on a vacuum line, heated in an oil bath for the required period, then reattached to the vacuum line, and the contents transferred to a small sampling tube to which was added 20 μl of toluene; upon thorough mixing triplicate g.c. analyses of each tube were carried out using a 0.01 in. i.d. × 150 ft capillary column coated with β,β′-oxydipropionitrile. The ratio of toluene to **4** and **5** was essentially constant, whether the toluene was added before or after the heating, indicating that the vacuum transfers were essentially quantitative. Table 3 gives the equilibrium data obtained and Fig. 1 shows a plot of the log K *vs.* $1/T$. A least-squares calculation gives $\Delta H = -5.18 \pm 0.15$ kcal mol^{-1} and $\Delta S = +1.44 \pm 0.21$ e.u. for the conversion of **5** to **4**.

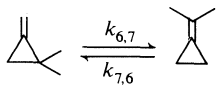
Kinetic data for the conversion of **5** → **4** are given in Table 4 along with the activation parameters for this isomerization. At 165.15° the equilibrium constant, $K = k_{5,4}/k_{4,5}$, extrapolated from the data in Table 3, has a value of 793, thus the process measured is essentially that of $k_{5,4}$ since $k_{4,5}$ is $0.0012k_{5,4}$. For comparison purposes we have examined the equilibrium between 2,2-dimethylmethylenecyclopropane (**6**) and isopropylidenecyclopropane (**7**),

TABLE 5. Equilibrium data for **6** ⇄ **7** at various temperatures (K = [**7**]/[**6**])

Temperature (°C)	Reaction time (h)	%**6** at equilibrium	K
220.30±0.02	72	21.34±0.04[a]	3.68±0.01
236.25±0.03	36	22.02±0.06	3.54±0.01
253.21±0.04	12	22.64±0.10	3.41±0.02
272.33±0.08	12	23.32±0.15	3.29±0.03
285.32±0.08	8	23.77±0.09	3.21±0.02

[a]Error listed in the standard deviation of nine analyses, triplicate determinations on each of three samples.

materials available to us from an accompanying study (1). Table 5 gives the equilibrium data obtained. A least squares calculation gives $\Delta H = -1.17 \pm 0.07$ kcal mol^{-1} and $\Delta S = 0.22 \pm 0.10$ e.u. for the isomerization of **6** to **7**. Measurement of the specific reaction rate constants, between **6** and **7**, in the gas phase (300 Torr) gave $k_{6,7} = (8.38 \pm 0.12) \times 10^{-6}$ s^{-1} and $k_{7,6} = (2.11 \pm 0.03) \times 10^{-6}$ s^{-1} at 190.10 ± 0.02°.



6 **7**

Experimental

The n.m.r. spectra were recorded on Varian A-60 and A-100 analytical spectrometers. The analytical gas chromatography was carried out using a Perkin-Elmer 900GC equipped with capillary columns and a Hewlett Packard 3370A Electronic Integrator. Mass spectra were determined on an AEI MS-9 double focusing high resolution spectrometer.

3,3,5,5-Tetramethyl-4-pyrazolidone

A solution of 2,4-dibromo-2,4-dimethyl-3-pentanone (135 g, 0.5 mol) (3) in ethanol (100 ml) was added slowly to a stirred solution of 64% hydrazine hydrate (105 ml, 1.3 mol N_2H_4) in ethanol (500 ml) along with 0.2 g of EDTA. Upon completion of addition the flask was warmed, with occasional swirling of the contents, on the steam bath for 1 h. The hydrazine hydrobromide, which precipitated upon cooling, was removed by suction filtration and the filtrate reduced to approximately one third its original volume. On cooling, the solution produced 19.5 g (27%) of white crystals, m.p. 115–117° (dec.), an additional 5 g was obtained by concentration of the mother liquor. The yield from this preparation varied from 20 to 50%.

A good microanalysis of this compound was not obtained. The percentage hydrogen was always lower than expected as the sample was always contaminated with some of the oxidation product **3**.

The n.m.r. spectrum, δ TMS ($CDCl_3$) 1.15 (sharp singlet, 12 H) and 3.61 (broad signal, NH, 2H). Traces of **3** were present as evidenced by a singlet at δ 1.33 (see the following preparation).

3,3,5,5-Tetramethyl-1-pyrazolin-4-one (3)

A mixture of 3,3,5,5-tetramethyl-4-pyrazolidone (5 g, 35 mmol) and active manganese dioxide (6.2 g, 71 mmol) (4) in pentane (400 ml) was shaken in pressure bottles for 24 h. After filtration the solution was concentrated to 25 ml and refrigerated. The product consisted of 2.7 g (55%) of white crystals which on sublimation gave m.p. 83.5–85°.

Anal. Calcd. for $C_7H_{12}N_2O$: C, 59.97; H, 8.63; N, 19.98. Found: C, 59.60; H, 8.56; N, 19.78.

The n.m.r. spectrum, δ TMS (CCl_4) displayed a single peak at 1.33; u.v. (ethanol) λ_{max} 356 nm (log ε 2.18); i.r. (CCl_4) cm^{-1}, strongest peaks at 2990, 2940, 1760, 1468.

3,3,5,5-Tetramethyl-4-methylene-1-pyrazoline(1)

Sodium hydride (167 mmol; 7.1 g as a 57% dispersion in mineral oil) was added to a 500-ml three-necked flask fitted with a reflux condenser, gas inlet tube, and magnetic stirrer. The mineral oil was removed by washing with dry *n*-pentane (3 × 200 ml). The last of the *n*-pentane was removed by evacuating the flask and then dimethyl sulfoxide (150 ml) was added and warmed to 80° for 1 h. Upon cooling triphenylphosphonium bromide (59.5 g, 0.167 mol) was added to the resulting solution of the methyl sulfinyl carbanion. Upon completion of addition the solution was warmed to 60° for 1 h. A sample of **2** (15.0 g, 107 mmol) was added and the solution stirred at 55° overnight. The reaction mixture was then poured into water (4 l) and the triphenylphosphine oxide removed by filtration. The precipitate was washed, and the filtrate extracted, with pentane (3 × 1 l). The combined extracts were dried over anhydrous sodium sulfate and concentrated to 50 ml and the residual crystals sublimed at one atmos. and 50° to give 11.2 g (76%) of crystals m.p. 35.0–36.2° (lit. (2) 34.5–35.5°). The n.m.r. spectrum, δ TMS ($CDCl_3$) 5.00 (singlet, 2H) and 1.42 (singlet, 12H); u.v. (CH_3OH) λ_{max} 328 nm (log ε 2.24).

Preparation of 4 and 5 by the Photolysis of 1

A *n*-pentane (150 ml) solution of **1** (6.5 g, 47 mmol) was photolyzed at 0 °C using Pyrex-filtered light from a 450 W Hanovia high pressure mercury lamp. The reaction was followed by g.c. (SE 30 column, 0.25 in. i.d. × 5 ft) and required 72 h for 98% conversion. During the photolysis the ratio of **5**:**4** stayed constant at 57:43. Upon completion the reaction mixture was concentrated to 30 ml using a spinning band column and the residue was subjected to preparative g.c. using a 10 ft × 0.25 in. column of UCW 98 (flow rate 40 ml/min, room temperature).

The n.m.r. spectrum of **4**, δ TMS ($CDCl_3$) 1.74 (broad singlet, 6H) 1.14 (singlet, 6H) 0.79 (singlet 2H). Exact mass calcd. for C_8H_{14}: 110.1096; found: 110.1096.

The n.m.r. spectrum of **5** δ TMS ($CDCl_3$) 5.14 (singlet, 2H) 1.12 (singlet, 12H). Exact mass calcd. for C_8H_{14}: 110.1096; found: 110.1096.

Kinetic Measurements

Thermolysis of 1

Pyrex break-seals (18 mm diameter and 70 mm long) were attached to a vacuum line and were evacuated and flamed before filling. A sample of **1** (25–30 mg), such as to give 300 Torr at 200°, was transferred to each break-seal and the sample removed from the vacuum line. Kinetic runs were made by immersing the break-seals in a well-stirred, thermostatted, silicone oil bath for the appropriate length of time and then quickly quenching the samples in ice water. The break-seals were then reattached to the vacuum line and the contents vacuum transferred to a sample vial (5 mm diameter, total length 45 mm) attached to the vacuum line by a carefully ground 5/20 joint. Each sample was analyzed in triplicate using a 150 ft × 0.01 in. diameter capillary column at 50°. Transfers were shown to be quantitative by the addition of toluene as an internal reference at the initial filling and at the sampling stage. An example of the analytical data is given in Table 1.

Rate of Isomerization of 4 and 5

Samples of **5** (10 μl, 99.87 ± 0.01% pure) were transferred to break-seals which were attached to the vacuum line, degassed, and sealed. After heating for the appropriate period in a well stirred, thermostatted, silicone oil bath the break-seals were reattached to the vacuum line and the product handled in the same manner as described for the kinetics of the thermolysis of **1**. The reaction was demonstrated to be first order by a set of tubes wherein 2, 10, and 30 μl of sample were used in tubes of the same volume, and no difference in the ratio of **4**:**5** could be detected when they were heated for an identical period of time.

Equilibration of 6 and 7

Samples of pure **6** and pure **7** were obtained by the thermolysis of 3,3-dimethyl-4-methylene-1-pyrazoline (1) followed by preparative g.c. separation using a 20 ft × 0.25 in. i.d. column of β,β′-oxydipropionitrile at 25°. The equilibration studies were carried out in a manner analogous to that described for **4** except that chloroform was used as an internal reference and the g.c. analyses were carried out using a 150 ft × 0.01 in. capillary column coated with β,β-oxydipropionitrile. Triplicate analyses were carried out on each tube and three tubes were examined at each temperature.

Discussion

It is apparent from Table 1 that the product proportions, as represented by the ratio **5**:**4**, decrease throughout the reaction. From Tables 2 and 4, at 165°, it can be seen that **5** is isomerizing to **4** at least eight times faster than it is being produced from **1**. This prevents the direct observation of our principal objective, which is the initial ratio of **5**:**4** and thus we have attempted to assess this ratio on the basis of kinetic data.

The concentration of **1**, C_1, at any time, t, during the reaction is given by the equation:

$$[1] \qquad C_1 = C_1{}^0 C^{-k_s t}$$

where $k_s = k_{1,4} + k_{1,5}$, and the concentration of **5** is given by eq. 2.

$$[2] \quad dC_5/dt = k_{1,5}C_1 + k_{4,5}C_4 - k_{5,4}C_5$$

From Table 3 we see that $k_{4,5}$ is small and that the rate, $k_{4,5}C_4$, is such that we can treat the system as an irreversible process. Rearranging eq. 2 and substituting for C_1 from eq. 1 we get:

$$[3] \qquad dC_5/dt + k_{5,4}C_5 = k_{1,5}C_1{}^0 e^{-k_s t}$$

Equation 3 is a linear differential equation with constant coefficients. Its solution is:

$$[4] \qquad C_5 = \frac{k_{1,5}C_1{}^0}{(k_{5,4} - k_s)}(e^{-k_s t} - e^{-k_{5,4}t})$$

A plot of the concentration of **5** at time t *vs.* $(e^{-k_s t} - e^{-k_{5,4}t})$ gives a straight line of slope $(k_{1,5}C_1{}^0)/(k_{5,4} - k_s)$ from which we can calculate the value of $k_{1,5}$. Using the data in Table 1 and a least-squares fit for eq. 4 we obtain $(3.92 \pm 0.26) \times 10^{-5}$ s^{-1} for $k_{1,5}$. The percentage of **1** that is converted directly to **5** is 49 ± 3%. Similar calculations at 165.15 and 200.11° give 50.5 ± 0.7 and 51.3 ± 1.0%. The amount of **5** present, upon the thermolysis of a sample of **1**, for 15 min at 165.17°, was 49.4 ± 0.2% of the C_8H_{14} product. Correction to zero conversion suggests that the ratio $k_{1,5}/k_s$ is 0.524 ± 0.003.

Table 6 lists the activation parameters for those 4-alkylidene-1-pyrazolines which have been studied in the gas phase. While the span of relative rates is not large the surprising factor is that the replacement of hydrogen by methyl slows down the rate. This is not what is normally expected, and it can be seen from Table 6 that **1** is one third the rate of 3,3,5,5-tetramethyl-1-pyrazoline (**12**), thus there appears to be no acceleration from the allylic nature of the incipient radical. We can only surmise that the bulkier methyl groups have prevented any manifestation of the allylic nature and suggest that the cleavage of the carbon–nitrogen bond(s) in **1** is occurring in the plane of the ring. Professor Paul Engel has informed us of similar kinetic parameters observed for the thermolysis of 3,3,5,5-tetra-

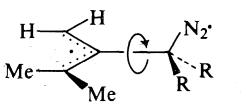
TABLE 6. The relative rates, at 160.17°, and activation parameters for the gas phase thermolysis of some 4-alkylidene-1-pyrazolines and for 3,3,5,5-tetramethyl-1-pyrazoline

Compound	E_a (kcal mol^{-1})	log A	$\Delta S_{200}^{\neq}$ (e.u.)	Relative rate	Reference No.
 **8**	32.6 ± 0.3	13.24	−1.1	62.8	1
 **1**	40.7 ± 0.4	15.53	+9.8	1.0	This work
 **9**	39.8 ± 0.6	13.6	+0.7	0.031	[a]
 **10**	—	—	—	21	1
 **11**	—	—	—	24	1
 **12**	37.7 ± 0.4	14.49	4.6	3.0	5

[a]Private communication from Prof. P. Engel, Department of Chemistry, Rice University, Houston, Texas.

methyl-4-isopropylidene-1-pyrazoline (**9**). This suggests that neither **1** nor **9** can fold to an envelope conformation analogous to cyclopentene and other 1-pyrazolines (6). It is apparent however that **1** and **9**, have sufficiently different activation parameters from those observed for **8** that the transfer of mechanistic constraints, based on kinetics, must be severely restricted.

Although we cannot readily characterize the transition state for the thermolysis of **1** relative to 4-methylene-1-pyrazoline we can compare the product distributions from **1**, **10**, and **11**. If the initial step consists of breaking a carbon–nitrogen bond then the allylic diazenyl[1] species **13** will be produced. The products can then arise via a displacement of nitrogen by either of the allylic termini in a mechanism analogous to that suggested by Roth and Martin (7) for bicyclic azo compounds. This may be controlled by the rotational conformations of **13**, which vary as we go from R = H to R = CH_3, thus rationalizing



13

a R = Me

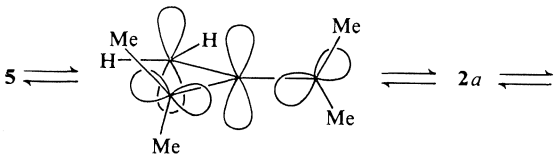
b R = H

why the ratio of **6**:**7** (63:37) from **11** is different from that of observed for **5**:**4** (52:48) from **1**.

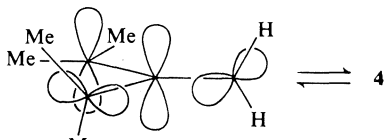
If the nitrogen is lost from the hydrocarbon residue either in the rate determining step, or in a rapid subsequent step, then the Chesick (8) intermediate **2** is produced, and we must ask why is the isopropylidene group only slightly faster (1.10 times at 165°) than the methylene group, whereas for **2***b* it is 1.70 times faster in rotating out of the allylic plane. If **2***a* and *b* are intermediates in the thermolysis of **1** and **11** then the rotational propensities exhibited are altered by the nature of the orthogonal radical center. These rotational propensities are different from the rotational preferences (R_A) observed by Doering and Sachdev (9) from

[1]While this bypasses some of the mechanistic constraints implied by **8** (1) it is not in serious conflict with the small increase in rate on going from **10** to **1**.

studies on the isomerization of cyclopropanes. The nature of the incipient π bond and the relative stability of the rotating radical center can affect the propensities shown herein and raise complications from which Doering's R_A values are free. An estimate of the geometry of the transition state for an intermediate such as **2***a* going to a product may be obtained by examining the alkylidenecyclopropane rearrangement of **5** ⇄ **4**. Assuming that the transition state is best represented by the extension of the cyclopropyl bond we have Scheme 1. The near equivalence of products



TS_1



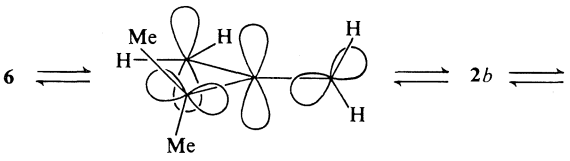
TS_2

$\delta\Delta G(TS_1 - TS_2) = -0.09$ kcal/mol^{-1}

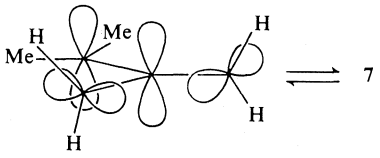
SCHEME 1

5 and **4** from **1** then suggests that $\delta\Delta G^{\ddagger}$ for TS_1 and TS_2 is essentially zero.

The isomerization **6** ⇄ **7** and their production from **11** via **2***b* give Scheme 2 wherein a free energy difference ($\delta\Delta G^{\ddagger}$) of 0.49 kcal mol^{-1} is observed for $TS_3 - TS_4$. The similarity of the free energy ($\Delta G^{\ddagger}$) changes on going from **4** → TS_2 (40.1 kcal mol^{-1} at 190°) and from **7** to TS_4 (39.5 kcal mol^{-1} at 190°) suggests that these two processes are very similar, whereas the free energy change on going from **5** to TS_1 (34.1 kcal mol^{-1} at 190°) and that on going from **6** to TS_3 (37.8 kcal mol^{-1} at 190°) are quite different.[2] This suggests that the



TS_3



TS_4

$\delta\Delta G(TS_3 - TS_4) = -0.46$ kcal/mol^{-1}

SCHEME 2

lower rotational propensity of the isopropylidene group in **2***a* relative to that in **2***b* comes from the steric factors in TS_1, and that even though the cyclopropane bond is stretched to near-breaking the steric factors which destabilize **5** are still manifested, although significantly attenuated.

Only by examining additional 4-alkylidene-1-pyrazolines can we decide whether the thermolysis of **8** is misleading and the intermediates such as **2** or **13** are involved. The decision between the intermediates **2** or **13** must also await further experimentation but the use of chiral 4-alkylidene-1-pyrazolines can resolve this question. We are continuing to explore the thermolysis of these systems.

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[2]An alternative way of stating this is to point out that at 190° the rate at which the ring methylene of **4** becomes the *exo*-methylene of **5** is 2.14 × 10^{-6} s^{-1} at 190°, and for a ring methylene of **7** to become the *exo*-methylene of **6** is 1.11 × 10^{-6} s^{-1}, both very comparable. The rate at which the *gem*-dimethyl of **7** becomes the isopropylidene of **6** is 8.38 × 10^{-6} s^{-1} at 190°, and for a *gem*-dimethyl of **5** to become the isopropylidene of **4** is 6.15 × 10^{-4} s^{-1}. The free energy changes above are then corrected for by the $\delta\Delta G^{\ddagger}$ values of Schemes 1 and 2.