Experimental Determination of the Relative Rates of Rotation, Cleavage, Closure, and 1,5-Hydrogen Shift for 3-Methyl-1,4-pentanediyl. Evidence for 1,4 Biradicals as Common Intermediates from Different Precursors, 3,4-(and 3,6-)Dimethyl-3,4,5,6-tetrahydropyridazines and 1,2-Dimethylcyclobutanes[1,2]

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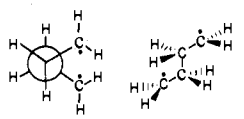
Abstract: Thermal decomposition of *cis*- and *trans*-3,6-dimethyl-3,4,5,6-tetrahydropyridazine (**11** and **12**, respectively) affords propene, *cis*- and *trans*-1,2-dimethylcyclobutanes, and 1-hexene. The stereochemistry of the products is consistent with a 1,4-biradical intermediate(s) 2,5-hexanediyl, which has the properties k(rotation) ~ k(cleavage) ~ k(closure). At 439 °C the retention/inversion (r/i) ratios for the 1,2-dimethylcyclobutane products are 1.7 and 1.7 from **11** and **12**, respectively. At 306 °C, these ratios are 1.9 and 2.2, respectively. The results indicate that when the thermal reactions of cyclic azo compounds and cyclobutanes of similar substitution are compared at similar temperatures, the stereospecificities are similar. We conclude that stereoretention is dependent on both substitution and temperature, i.e., stereospecificity increases as substitution at the radical center increases and as the temperature is lowered. The thermal decomposition of *cis*- and *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazine (**19** and **20**, respectively) allows a dissection of direct vs. 1,4-biradical pathways in six-membered cyclic azo decompositions, e.g., 36% direct/64% 1,4 biradical from *cis*-**19** and 32% direct/68% 1,4 biradical from *trans*-**20**. The relative rates of rotation, cleavage, and closure for azo-generated 1,4 biradicals, 3-methyl-1,4-pentanediyl (**8T** and **8C**), were determined. For **8T**, k(cleavage)/k(closure) = 1.6 and k(closure)/k(rotation) = 1.9. For **8C**, k(cleavage)/k(closure) = 1.8 and k(closure)/k(rotation) = 0.7. These relative rates of rotation, cleavage, and closure generate similar *trans*-/*cis*-2-butene ratios as found in the pyrolyses of *cis*- and *trans*-1,2-dimethylcyclobutanes at the same temperature and phase. We conclude they pass the stereochemical test for identity, indicating evidence for common 1,4-biradical intermediates from two different precursors (1,2-diazenes and cyclobutanes). Finally, the data are compared with the recent literature values reported for the dimerization of ethylene and 2-butenes.

Introduction

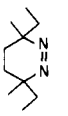
Experimental work has shown that many thermal and photochemical reactions do not take advantage of cyclic transition states, but apparently proceed via simple bond broken species or biradicals.[4,5] In this paper we test whether certain biradicals generated from different precursors are *common* intermediates on some energy surface, i.e., have identical stereochemical behavior. Variables such as temperature, phase, and substituents affect the behavior of biradical intermediates. In tests for commonality of biradical intermediates where these variables are not the same, the outcome usually shows different stereochemical behavior. Because of its size, simplicity, and theoretical importance, we have chosen to study the 1,4 biradical.[6-12]

Hoffmann's extended Hückel (EH) calculation for the energy surface between cyclobutane and two molecules of ethylene revealed a rather flat hypersurface.[6b] Segal concluded from an ab initio calculation (SCF at STO-3G level) that there are two well-defined potential energy minima for the gauche and trans conformations of tetramethylene.[6f] The barriers to cleavage and closure for *gauche*-tetramethylene are 3.6 and ≥2.0 kcal/mol, respectively. Benson's thermochemical estimates predict similar differences between the heats of formation of the transition states for cleavage and closure from tetramethylene but a deeper well.[5]



1 *gauche* 2 *trans*

In 1961, Gerberich and Walters studied the pyrolyses of *cis*- and *trans*-1,2-dimethylcyclobutanes in the gas phase at 425 ± 25 °C.[7b] The products were consistent with the intermediacy of 1,4 biradicals where rotation is competitive with cleavage and closure.[5] Cyclic azo compounds (or 1,2-diazenes) are considered good routes for the generation of biradicals.[9] In 1969, Bartlett and Porter studied the thermal decomposition of *meso*- and *dl*-3,6-diethyl-3,6-dimethyltetrahydropyridazines (**9**) in solution at 150 °C.[9a] The highly stereospecific



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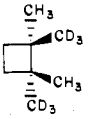

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formation of the isomeric cyclobutanes was consistent with a 1,4-biradical where k(rotation) ≪ k(cleavage) and k(closure). This increased stereospecificity with respect to the 1,2-dimethylcyclobutane system could reasonably be ascribed to slower rotation in the tertiary radical center vs. secondary radical center due to increased rotational barriers in the more highly substituted system. However, the importance of phase (solution vs. gas), temperature (150 vs. 425 °C), and method of generation (1,2-diazene vs. cyclobutane) could not be separated out. Brauman and Stephenson suggested that differences in behavior might be due to differences in the method of generation.[13] For example, the 1,2-diazene route to biradicals might provide intermediates of similar structure but different energy. In 1970, Berson, Tomkin, and Jones showed that, for a highly substituted cyclobutane (**10**) which on thermal decomposition would afford a biradical with tertiary radical centers, k(rotation) ≪ k(cleavage), consistent with the view that stereoretention is not an intrinsic property but depends on substitution.[7e,f]

We report here experiments in which three variables are kept

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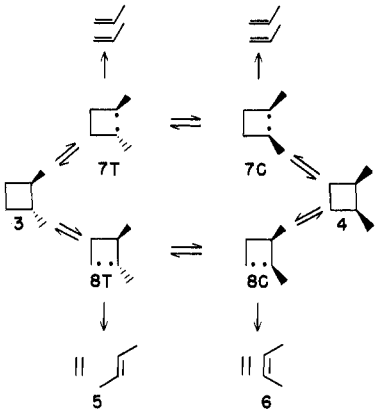
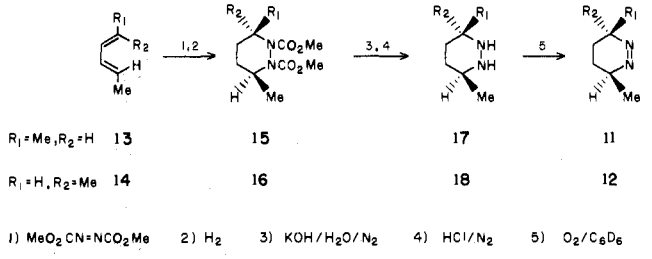
Scheme I



Scheme II



the same (e.g., phase, temperature, substitution) and only the mode of generation is different. Secondary radical centers are expected to afford more product crossover than tertiary radical centers, and hence will be a sensitive test. The 1,2-dimethylcyclobutane system is sufficient for one method of generation.[7b] In this study, both propene and 2-butene products were observed, indicating that this system is complicated by the intermediacy of two different sets of 1,4 biradicals (Scheme I). The relative rates of rotation, cleavage, and closure for 2,4-hexanediyl (**7**) and 3-methyl-1,4-pentanediyl (**8**) could not be determined directly.

We describe efforts to generate 1,4 biradicals by the thermal decomposition of 1,2-diazenes with identical substitution as the species from the cleavage of *cis*- and *trans*-1,2-dimethylcyclobutanes at the same temperature and phase. The only variable will be the method of generation and the test for identity can be applied. This allows direct determination of the relative rates of rotation, cleavage, and closure for a 1,4 biradical. The data will then be compared with the *cis*- and *trans*-1,2-dimethylcyclobutane decomposition studies.

Results and Discussion

Synthesis and Thermal Decomposition of *cis*- and *trans*-3,6-Dimethyl-3,4,5,6-tetrahydropyridazines (11 and 12, Respectively). Diels–Alder addition of *trans,trans*- and *cis,trans*-hexa-2,4-diene to dimethyl azodicarboxylate, followed by hydrogenation, afforded the *cis*- and *trans*-diurethane precursors **15** and **16**, respectively, 99 and 97% isomerically pure. Hydrolysis of the diurethanes followed by decarboxylation was carried out under an inert atmosphere (N_2) using thoroughly degassed solvents. The *cis*- and *trans*-hydrazine products **17** and **18**, respectively, were distilled on a vacuum line (10^{-4} Torr). Oxidation of the pure hydrazines in benzene-d_6 to the corresponding azo compounds **11** and **12** was accomplished by treatment with oxygen and monitored by NMR (Scheme II). For pyrolysis, these solutions were injected into an evacuated Pyrex chamber (preheated to 306 or 439 °C) and the products were collected in a trap at −196 °C. The product ratios were determined by electronically integrated analytical vapor phase chromatography (VPC) analysis (see Table I).

Table I

reactant	conditions	% yields[a] 2			
cis-**11**	*b*	74.7	8.5	16.3	0.5
	c	72.9	9.7	16.3	1.1
trans-**12**	*b*	80.5	12.7	5.7	1.1
	c	74.4	14.9	8.9	1.8

[a] Percent yield based on total hydrocarbon product. Typical absolute yields of hydrocarbon products from **11** and **12** were 50 and 80% at 306 and 439 °C, respectively. VPC analysis using 30 ft × ⅛ in. 10% dibutyl tetrachlorophthalate; flame ionization detector. [b] Chamber pyrolysis (30 s at 306 ± 2 °C, estimated pressure >25 mm). [c] Chamber pyrolysis (5 s at 439 ± 2 °C, estimated pressure >31 mm).

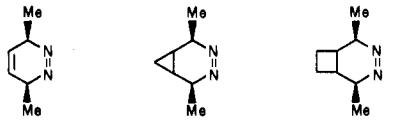
Table II. Retention/Inversion Ratios (*r/i*) in the Cyclobutane Closure Products

	temp, °C	phase	*r/i*
meso-**9**	148	solution	49
dl-**9**	148	solution	49
cis-**11**	306	gas	1.9
trans-**12**	306	gas	2.2
cis-**11**	439	gas	1.7
trans-**12**	439	gas	1.7

The thermal decompositions of *cis*- and *trans*-3,6-dimethyl-3,4,5,6-tetrahydropyridazines (**11** and **12**) afford propene, 1,2-dimethylcyclobutanes, and 1-hexene. Examination of the stereochemistry of the 1,2-dimethylcyclobutane products reveals that, although overall retention is preserved, the loss of stereochemistry in the closure products is relatively high. If 1,4 diradicals with secondary radical centers intervene in these azo decompositions (**11** and **12**), the data indicate that carbon–carbon bond rotation is competitive with cleavage and closure. Thus, the intermediates formed from azo compounds **11** and **12** are similar in behavior to those from the thermal decomposition of *cis*- and *trans*-1,2-dimethylcyclobutanes. We have the qualitative finding that substitution and temperature, not mode of generation, determine the stereochemical behavior of the 1,4 biradicals.

Examination of the stereochemistry of the azo-generated ring closure products reveals that the retention/inversion ratios (*r/i*) are sensitive to both substitution and temperature; i.e., stereospecificity increases as substitution at the radical center increases and as the temperature is lowered (Table II). These results emphasize that valid comparison between thermally generated species from different precursors must involve structures of similar substitution at the same temperature.

Synthesis and Thermal Decomposition of *cis*- and *trans*-3,4-Dimethyl-3,4,5,6-tetrahydropyridazenes (19 and 20), Respectively. The thermal decomposition of a differently substituted azo precursor provides information on the cleavage stereochemistry in the six-membered cyclic azo system. Berson and co-workers have shown kinetic and stereochemical evidence that six-membered cyclic azo compounds with a π or bent σ backbone bond, **21–23**, undergo what appears to be



21 22 23

concerted (2 + 2 + 2) cycloreversions with the degree of concert diminishing as the backbone bond orbital acquires more σ character.[15c] A question that remains unanswered is whether some degree of concert is left (path a, Scheme III) if the backbone bond were pure σ. In order to measure directly the relative rates of rotation, cleavage, and closure for a 1,4 biradical from the corresponding azo precursor, any direct component (path a) of cleavage product superimposed on the 1,4-biradical pathway (path b) from the azo decomposition must be separated (Scheme III).

Analyses of the products from the thermal decomposition of *cis*- and *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazines (**19** and **20**) allow one (a) to test whether ring-closure and all fragmentation products in six-membered cyclic azo fragmentations arise from a common 1,4-biradical intermediate(s), (b) to determine the relative rates of rotation, cleavage, and closure of 3-methyl-2,5-pentanediyls (**8**), and (c) to test for any trace of (2 + 2 + 2) cycloreversion in a "pure σ" six-membered cyclic azo decomposition.

The stereospecific syntheses of the 3,4-substituted tetrahydropyridazines **19** and **20** were accomplished in the following manner (see Scheme IV). Hydroboration of 3-methyl-*cis*-(and *trans*-)1,3-pentadienes (**25** and **24**), followed by oxidation, afforded *erythro*-(and *threo*-)3-methylpentane-1,4-diols (**27** and **26**).[16] Reaction of the corresponding *erythro*-(and *threo*-)diol dimethanesulfonates (**27** and **26**) with dimethylhydrazo-1,2-dicarboxylate and sodium hydride afforded dimethyl *trans*-(and *cis*-)3,4-dimethyltetrahydropyridazine-1,2-dicarboxylates (**29** and **28**). These *cis*- and *trans*-diurethanes **28** and **29** were further purified by preparative vapor phase chromatography (VPC) (>99.5% isomeric purities). Hydrolysis of the diurethanes followed by decarboxylation was carried out under an inert atmosphere (N_2) using thoroughly degassed solvents and the *cis*-(and *trans*-)hydrazine products **30** and **31** were distilled on a vacuum line (10^{-4} Torr). Oxidation of the pure hydrazines in benzene-d_6 to the corresponding azo compounds **19** and **20** was accomplished by treatment with oxygen and monitored by NMR. These azo compounds **19** and **20** are sensitive and suffered facile irreversible azo to hydrazone tautomerization in the presence of trace amounts of acid, base, and light. For pyrolyses, these solutions were injected into an evacuated Pyrex chamber (preheated to 306 or 439 °C) and the products were collected in a trap at −196 °C. The product ratios were determined by electronically integrated analytical vapor phase chromatography (VPC) analysis.

The dominant processes that appear to be occurring in these azo-derived 1,4 biradicals are rotation, cleavage, and closure (Table III). Under analytical conditions reported in a preliminary account of this work,[6d] we were not able to detect 3-methyl-1-pentene (**32**), the expected hydrogen-shift product. However, we have repeated this work and scrutinized the products under several analytical VPC conditions. We find less than a few percent 3-methyl-1-pentene (**32**), not enough to change significantly the relative rates of rotation, cleavage, and closure, but a sufficient amount to give us some idea of the relative competitiveness of the hydrogen shift process.

Scheme III

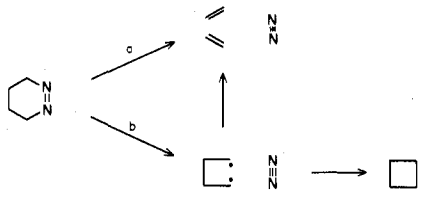
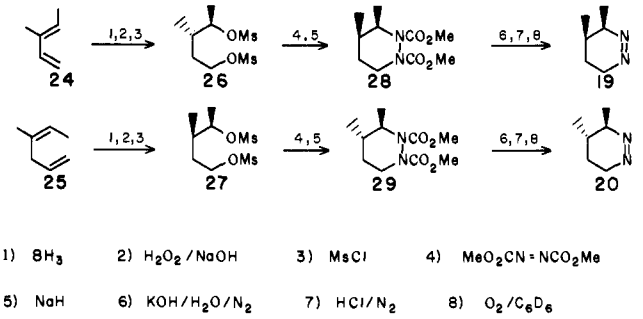


Table III

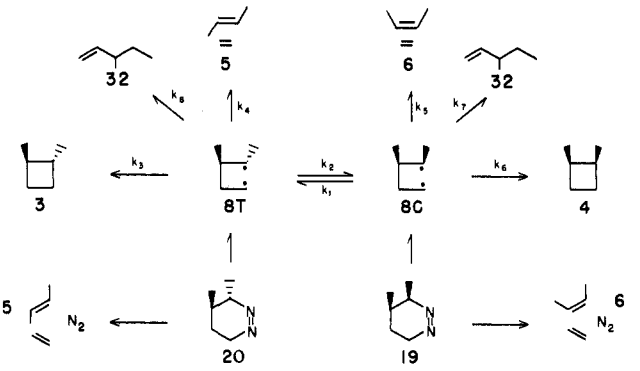
reactant	conditions	% yields[a]				
						
cis-**19**	*b*	11.2	69.5	4.0	14.6	0.7
	c	11.4	64.4	7.0	16.0	1.2
trans-**20**	*b*	69.7	4.3	22.8	2.6	0.6
	c	68.7	5.2	22.5	2.9	0.7

[a] Percent yield based on total hydrocarbon product. Typical absolute yields of hydrocarbon products from **5** and **6** were 50 and 80% at 306 and 439 °C, respectively. VPC analysis using 20 ft × 1/8 in. 10% β,β'-oxydipropionitrile; flame ionization detector. [b] Chamber pyrolysis (30 s at 306 ± 2 °C, estimated pressure >25 mm). [c] Chamber pyrolysis (5 s at 439 ± 2 °C, estimated pressure >31 mm).

Scheme IV



Scheme V



Examination of the data reveals that the ratio of *trans*-2-butene/*trans*-1,2-dimethylcyclobutane is higher from the trans azo precursor **20** than from the cis azo precursor **19** (at 439 °C, 3.0 vs. 1.6). Similarly, the ratio of *cis*-2-butene/*cis*-1,2-dimethylcyclobutane is higher from the cis azo precursor **19** than from the trans azo precursor **20** (at 439 °C, 4.0 vs. 1.8). Thus, there is an extra component of stereospecific cleavage of retained stereochemistry from each azo compound.

Consider the following kinetic scheme (Scheme V). For the present we will ignore the small amount of 3-methyl-1-pentene (**33**), the hydrogen-shift product. However, it can be shown that from **8C**, k_2(H shift)/k_6(closure) = 0.065 and from **8T**, k_8(H-shift)/k_3(closure) = 0.023.

The ratio of k(cleavage)/k(closure) from each biradical (**8T** and **8C**) can be obtained directly from the azo decomposition products. Starting from trans azo **20** the ratio of crossover products *cis*-2-butene/*cis*-1,2-dimethylcyclobutane is the relative rates of unimolecular decomposition of biradical **8C**, k_5(cleavage)/k_6(closure) = 1.79. Similarly, starting from cis

Table IV

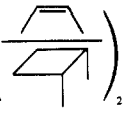
		
$k_4/k_3 = 1.63$	k(cleavage)/k(closure)	$1.79 = k_5/k_6$
$k_3/k_2 = 1.86$	k(closure)/k(rotation)	$0.72 = k_6/k_1$

azo **19,** the ratio of crossover products *trans*-2-butene/*trans*-1,2-dimethylcyclobutane is the relative rates of unimolecular decomposition of biradical **8T,** k_4(cleavage)/k_3(closure) = 1.63.

These k(cleavage)/k(closure) ratios, R_1 and R_2, and the cis/trans ratios of cyclobutane products, R_3 and R_4, observed from each azo isomer **19** and **20** will allow a determination of k(closure)/k(rotation) ratios from a simple steady-state analysis of the proposed diradical scheme (Scheme V).

Let R_1 and R_2 be the experimentally determined crossover cleavage/closure ratios:

$$R_1 = \left(\text{  }\right)_{19} = \frac{k_4}{k_3}$$

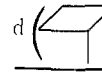
$$R_2 = \left(\text{  }\right)_{20} = \frac{k_5}{k_6}$$

From trans azo **20** using the steady-state assumption d(**8C**)/dt = 0:

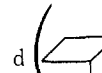
$$\frac{\mathrm{d}(\mathbf{8C})}{\mathrm{d}t} = k_2(\mathbf{8T}) - (k_1 + k_5 + k_6)(\mathbf{8C}) = 0$$

$$\frac{(\mathbf{8T})}{(\mathbf{8C})} = \left(\frac{k_1 + k_5 + k_6}{k_2}\right)$$

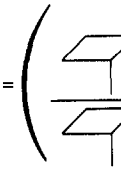
Since

$$\frac{\mathrm{d}\left(\text{  }\right)}{\mathrm{d}t} = k_6(\mathbf{8C})$$

and

$$\frac{\mathrm{d}\left(\text{  }\right)}{\mathrm{d}t} = k_3(\mathbf{8T})$$

then

$$R_3 = \left(\text{  }\right)_{20} = \frac{k_3(\mathbf{8T})}{k_6(\mathbf{8C})} = \frac{k_3}{k_6}\left(\frac{k_1 + k_5 + k_6}{k_2}\right)$$

$$R_3 = \frac{k_3}{k_2}\left(\frac{k_1}{k_6} + \frac{k_5}{k_6} + 1\right)$$

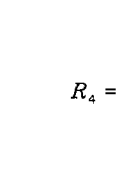
Let the k(closure)/k(rotation) ratios $k_3/k_2 = M$ and $k_6/k_1 = N$:

$$R = M\left(\frac{1}{N} + R_2 + 1\right)$$

From cis azo **19**, using the steady-state assumption d(**8T**)/dt = 0:

$$\frac{\mathrm{d}(\mathbf{8T})}{\mathrm{d}t} = k_1(\mathbf{8C}) - (k_3 + k_4 + k_2)(\mathbf{8T}) = 0$$

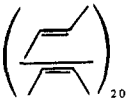
$$\frac{(\mathbf{8C})}{(\mathbf{8T})} = \left(\frac{k_3 + k_4 + k_2}{k_1}\right)$$

$$R_4 = \left(\text{  }\right)_{19} = \frac{k_6}{k_3}\frac{(\mathbf{8C})}{(\mathbf{8T})} = \frac{k_6}{k_3}\left(\frac{k_3 + k_4 + k_2}{k_1}\right)$$

$$R_4 = \frac{k_6}{k_1}\left(\frac{k_4}{k_3} + \frac{k_2}{k_3} + 1\right)$$

$$R_4 = N\left(R_1 + \frac{1}{M} + 1\right)$$

From the experimental data, $R_3 = 7.76$ and $R_4 = 2.29$. Solving for M and N, we find that $k_3/k_2 = 1.86$ and $k_6/k_1 = 0.72$. Therefore, from four experimental ratios from the VPC data of the azo pyrolyses (R_1 and R_4 from cis azo **19** and R_2 and R_3 from trans azo **20**) we determine the relative rates of rotation, cleavage, and closure for azo-derived 1,4 biradicals (Table IV). From these azo-derived rates of rotation, cleavage, and closure, we can calculate the *trans*-/*cis*-2-butene ratio expected from the trans azo derived biradical (**8T**) and the *cis*-/*trans*-2-butene ratio from the cis azo derived biradical (**8C**) and compare this to the experimentally observed ratios in the 1,2-dimethylcyclobutane decomposition:

$$\text{let } R_5 = \left(\text{  }\right)_{20} = \frac{k_4}{k_5}\frac{(\mathbf{8T})}{(\mathbf{8C})}$$

Then

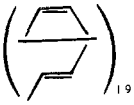
$$R_5 = \frac{k_4}{k_5}\left(\frac{k_1 + k_5 + k_6}{k_2}\right)$$

$$= \frac{k_4}{k_2}\left(\frac{k_1}{k_5} + 1 + \frac{k_6}{k_5}\right)$$

$$= 3.03\left(\frac{1}{1.29} + 1 + \frac{1}{1.79}\right)$$

$$R_5 = 7.08$$

R_5, the *trans*-/*cis*-2-butene ratio from the azo-generated 1,4 biradical, is 88/12. Similarly, we can calculate the ratio of *cis*-/*trans*-2-butene from the azo-derived 1,4 biradical using these same rates of rotation, cleavage, and closure:

$$R_6 = \left(\text{  }\right)_{19} = \frac{k_5}{k_4}\frac{(\mathbf{8C})}{(\mathbf{8T})}$$

$$R_6 = \frac{k_5}{k_4}\left(\frac{k_3 + k_4 + k_2}{k_1}\right)$$

$$R_6 = \frac{k_5}{k_1}\left(\frac{k_3}{k_4} + 1 + \frac{k_2}{k_4}\right)$$

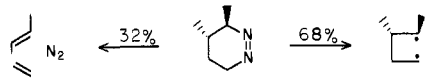
$$R_6 = 1.29\left(\frac{1}{1.63} + 1 + \frac{1}{3.03}\right)$$

$$R_6 = 2.51$$

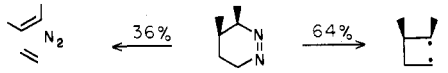
R_6, the *cis*-/*trans*-2-butene ratio expected for exclusive 1,4-biradical formation from the azo compound, is 72/28.

Recall that the experimental ratio of *trans*-/*cis*-2-butene from trans azo was 68.7/5.2. The calculated *trans*-2-butene should be only 7.08 times the *cis*-2-butene or (7.08 × 5.2 = 36.8). Therefore, the *extra* component of stereospecific cleavage superimposed on the azo-derived biradical is 68.7 − 36.8 = 31.9% (Scheme VI). Similarly, the experimental ratio

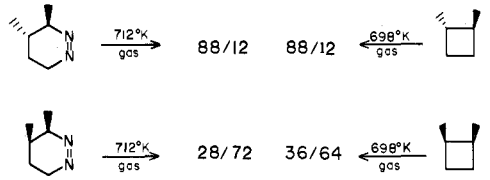
Scheme VI



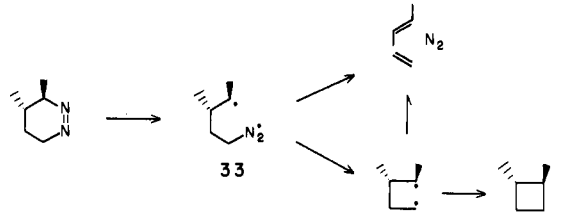
Scheme VII



Scheme VIII. Ratio of *trans*-/*cis*-2-Butenes Generated from Two Different Precursors



Scheme IX



of *cis*-/*trans*-2-butene from cis azo was 64.4/11.4. The calculated *cis*-2-butene from exclusive azo-derived biradical should be 2.51 × 11.4 = 28.6%. Therefore, the extra component of stereospecific cleavage superimposed on the azo-derived biradical is 64.4 − 28.6 = 35.8% (Scheme VII). In summary, the relative rates of rotation, cleavage, and closure for two azo-derived 1,4 biradicals, **8C** and **8T**, are determined from four experimental ratios from the decomposition products R_1 = 1.63, R_2 = 1.79, R_3 = 7.76, and R_4 = 2.29, and the steady-state assumption d(**8C**)/dt = 0 from trans azo **20** and d(**8T**)/dt = 0 from cis azo **19**. A comparison of the *trans*-/*cis*-2-butene ratios from the azo-derived biradicals and the cyclobutane-derived biradicals is shown in Scheme VIII.

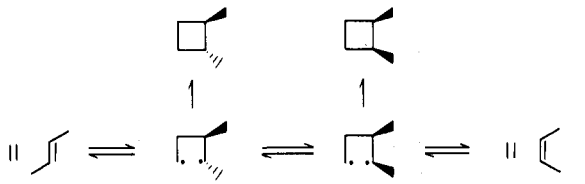
Since similar *cis*-/*trans*-2-butene ratios as found in the 1,2-dimethylcyclobutane pyrolyses are generated from the azo-derived relative rates of rotation, cleavage, and closure for 3-methyl-2,5-pentanediyl the *criterion of identity is satisfied.* This is evidence that biradicals or similar species are common points on an energy surface and can be generated from different points on that energy surface.

Moreover, an extra cleavage component superimposed on the 1,4-biradical pathway from a six-membered cyclic azo compound is now evident. Even in the pure σ system the direct 2 + 2 + 2 cycloreversion pathway, presumably a three-bond scission, is close in energy to the two-bond biradical pathway. ($\Delta\Delta G^{\ddagger} \simeq 0.8$ kcal mol^{-1} at 439 °C).

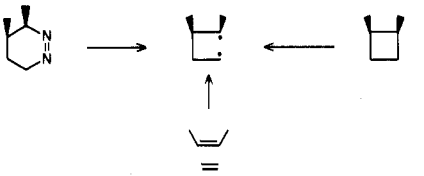
An alternative explanation to the three-bond vs. the two-bond mechanism is initial one-bond scission to a diazenyl radical **33**, which subsequently decomposes to olefin and 1,4-biradical competitively (Scheme IX). Since the analysis only distinguishes products of a direct stereospecific component from the 1,4-biradical component, the data do not permit a distinction between the 2 + 2 + 2 cycloreversion/1,4-biradical dual pathways occurring from the six-membered azo compound or a diazenyl fragmentation/1,4 biradical derived from the diazenyl radical **33**. One constraint on this diazenyl biradical is that it may not lose stereochemical integrity before decomposing to olefin or 1,4 biradical. Otherwise it would be fortuitous that the 1,4-biradical portion fits the dimethylcyclobutane pyrolysis data so well.

Recent evidence from a study of the cycloaddition of ethylene to 2-butene suggests a biradical(s) with behavior similar to the 1,2-diazene- and cyclobutane-generated species. Scacchi,

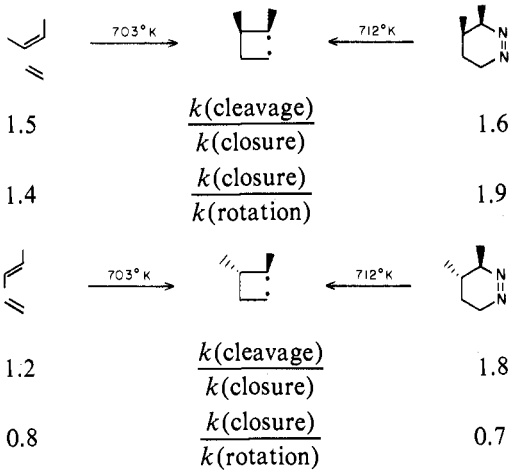
Scheme X



Scheme XI



Richard, and Bach have studied the thermal cycloaddition of ethylene to *cis*- and *trans*-2-butenes at 693 K at pressures of about 12 atm.[8c] Their results show that the cycloaddition reactions are the reverse of the decomposition reactions of 1,2-dimethylcyclobutanes and may be interpreted in terms of common biradical intermediates (Scheme X). They deduce ratios of rate constants for rotation, cleavage, and closure at 663, 678, 693, and 703 K from their data. A comparison of the Scacchi, Richard, and Bach analysis from the cycloaddition data and azo-derived ratios is shown below. The agreement is quite good.



Three different experiments which characterize the 3-methyl-1,4-pentanediyl are internally consistent (Scheme XI).

Both the cyclobutane and 1,2-diazene precursor can be reasonably assumed to generate the 1,4 biradical in a gauche (or cis) conformation. It is curious that the olefin dimerization[17] fits this data so well. We would conclude that either the olefins also dimerize in a gauche (or cis) conformation (rather than trans) or that rotation about the C_2–C_3 bond in the biradical is competitive with C_1–C_2 rotation. If the latter situation is occurring, an estimate of the C_2–C_3 rotational barrier (~3 kcal mol^{-1}) puts a lower limit on the C_1–C_2 rotational barrier for the biradical.[18] This is higher than what one might have expected from reported barriers to rotation (≤1.2 kcal mol^{-1}) in alkyl radicals.[19] Moreover, the stereospecificity of the biradical increases as the temperature is decreased. This is consistent with E_a(rotation) > E_a(cleavage) and E_a(closure) for 3-methyl-1,4-pentanediyl.

In summary, then, we have shown from the thermal decomposition of *cis*- and *trans*-3,6-dimethyl-3,4,5,6-tetrahydropyridazines (**11** and **12**, respectively) that stereoretention is dependent on both substitution and temperature, i.e., stereospecificity increases as substitution at the radical center increases and as the temperature is lowered. From the thermal

Table V. VPC Columns

column designation	description
DBT	20 ft × 0.125 in., 10% dibutyl tetrachlorophthalate on 100/120 Chromosorb P
FFAP	10 ft × 0.125 in., 10% FFAP on 100/120 Chromosorb W
Carbowax 20M	10 ft × 0.125 in., 10% Carbowax 20M on 100/120 Chromosorb W
ODPN	15 ft × 0.125 in., 10% β,β′-oxydipropionitrile on 100/120 Chromosorb P
Pennwalt	10 ft × 0.125 in., Pennwalt 223 amine packing (Applied Sciences Laboratories, Inc.)
FFAP	10 ft × 0.375 in., 25% FFAP on 60/80 Chromosorb W
ODPM	10 ft × 0.375 in., 25% β,β′-oxydipropionitrile on 60/80 Chromosorb P
Pennwalt	10 ft × 0.25 in., glass, Pennwalt 223 amine packing (Applied Sciences Laboratories, Inc.)

decomposition of *cis*- and *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazines we (a) measured the relative rates of rotation, cleavage, and closure for an azo-generated 1,4 biradical; (b) provided permissive evidence for *common biradical* intermediates generated from 1,2-diazene and cyclobutane route by keeping temperature, phase, and substitution the same; and (c) separated a direct cleavage component in a six-membered cyclic azo decomposition with a pure σ backbone.

Experimental Section

Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Infrared spectra (IR) were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Associates A-60A and are uncalibrated. Chemical shifts are given as parts per million (ppm) downfield from Me_4Si in δ units and coupling constants in hertz (Hz). Nuclear magnetic resonance data are reported in the order: chemical shift; multiplicity, s = singlet, d = doublet, t = triplet, m = multiplet; number of protons; coupling constants; assignment. Electronic spectra were recorded on a Cary Model 14 spectrophotometer.

For analytical vapor-phase chromatography (VPC), a Hewlett-Packard 5700A gas chromatograph, equipped with flame ionization detector and nitrogen carrier gas, was used. The 0.125-in. packed stainless steel columns used in this instrument are listed in Table V. Quantitative VPC analysis was accomplished using a Hewlett-Packard 3370A electronic digital integrator. For preparative VPC, a Varian Aerograph Model 920 instrument, equipped with thermal conductivity detector and helium carrier gas, was used. The 0.375-in. packed aluminum columns used in this instrument are listed in Table V.

Most reagent grade chemicals were used without further purification. Diglyme and tetrahydrofuran were distilled from lithium aluminum hydride, and pyridine from barium oxide.

Dimethyl *trans*-3,6-Dimethyltetrahydropyridazine-1,2-dicarboxylate (16). A solution of 3.25 g (14.1 mmol) of dimethyl *trans*-3,6-dimethyl-3,6-dihydropyridazine-1,2-dicarboxylate, mp 67–71 °C, in 50 mL of methanol was hydrogenated over 0.2 g of platinum oxide. The solution was filtered, concentrated, and distilled affording 3.05 g (93%) of the saturated diurethane **16:** bp 94–95 °C (0.6 mm); IR (CCl_4) 1713 (C=O); NMR ($CDCl_3$) δ 0.9–1.6 (m, 8), 1.20 (d, J = 6.5 Hz), 1.65–2.30 (m, 2), 3.76 (s, 6, J = 2.5 Hz), 3.95–4.65 (m, 2). Anal. Calcd for $C_{10}H_{18}N_2O_4$: C, 52.16; H, 7.88; N, 12.16. Found: C, 52.14; H, 7.80; N, 12.11.

Dimethyl *cis*-3,6-Dimethyltetrahydropyridazine-1,2-dicarboxylate (15). In a similar procedure to the trans isomer, 9.12 g (0.040 mmol) of dimethyl *cis*-3,6-dimethyl-3,6-dihydropyridazine-1,2-dicarboxylate was hydrogenated over platinum oxide to afford 7.3 g (80%) of the saturated diurethane **15:** bp 83 °C (0.1 mm); mp 44–45 °C; IR (CCl_4) 1712 (C=O); NMR ($CDCl_3$) δ 1.2 (d, 3, J = 7 Hz), 1.4–2.2 (m, 7), 1.55 (d, J = 7 Hz), 3.5–5.7 (m, 8), 3.7 (d, J = 4 Hz). Anal. Calcd for $C_{10}H_{18}N_2O_4$: C, 52.16; H, 7.88; N, 12.12. Found: C, 52.24; H, 7.93; N, 12.25.

***cis*-(and *trans*-)1,2,3,6-Tetramethylhexahydropyridazines (35 and 36, Respectively).** The isomeric dimethyl *cis*-(and *trans*-)3,4-dimethyltetrahydropyridazine-1,2-dicarboxylates (**15** and **16**) could not be separated conveniently by analytical gas chromatography. Although the synthesis of each isomer is expected to be stereospecific, a check on the isomeric composition was necessary. Conversion to the known *cis*-(and *trans*-)1,2,3,6-tetramethylhexahydropyridazines (**35** and **36**), separable by VPC, would allow this determination.

Lithium aluminum hydride reduction of dimethyl *cis*-(and *trans*-)3,4-dimethyltetrahydropyridazine-1,2-dicarboxylates (**15** and **16**) according to the procedures of Lehn afforded *cis*-(and *trans*-)-3,4-dimethyltetrahydropyridazines[19] of 97 and 99% isomeric purity, respectively (Pennwalt-223, 180 °C).

Dimethyl *trans*-3,4-Dimethyltetrahydropyridazine-1,2-dicarboxylate (29). To a solution of 5.5 g (31.2 mmol) of dimethylhydrazine 1,2-dicarboxylate in 50 mL of diglyme (distilled from lithium aluminum hydride) was added 1.5 g of sodium hydride (50% mineral oil dispersion, 31.2 mmol) under nitrogen atmosphere. After the evolution of hydrogen had stopped, a solution of 9.5 g (31 mmol) of *erythro*-3-methyl-1,4-pentanediyl-1,4-dimethanesulfonate in 30 mL of diglyme was added. The mixture was allowed to stir under reflux for 24 h. The solution was allowed to cool and 50 mL of diglyme and 1.5 g of sodium hydride were added. After heating under reflux for 24 h, the mixture was cooled and filtered. The filtrate was diluted with 25 mL of water and extracted with 200 mL of ether. The ethereal extract was dried ($MgSO_4$) and concentrated under reduced pressure. The remaining oil was washed with 30 mL of *n*-hexane. The residue was chromatographed over 30 g of silica gel to yield 714 mg of colorless oil (8.5%). The product was shown by analytical VPC (10% FFAP, 205 °C) to consist of 93.6% **29** and 6.4% **28.** This was further purified by preparative VPC (FFAP, 205 °C) affording **29,** >99.9% pure: IR ($CHCl_3$) 1698 (C=O); NMR ($CDCl_3$) δ 0.9–2.2 (m, 9), 1.06 (d, J = 6.3 Hz), 1.23 (d, J = 6.8 Hz), 2.9–4.4 (m, 9), 3.72 (s), 3.76 (s). Anal. Calcd for $C_{10}H_{18}N_2O_4$: C, 52.16; H, 7.88; N, 12.16. Found: C, 52.08; H, 8.01; N, 12.16.

Dimethyl *cis*-3,4-Dimethyltetrahydropyridazine-1,2-dicarboxylate (28). When a procedure identical with that used for the preparation of **29** was applied to *threo*-3-methyl-1,4-pentanediyl-1,4-dimethanesulfonate, the cis product **28** was obtained in 17% yield. The product was shown by analytical VPC (10% FFAP, 205 °C) to consist of 94% **28** and 6% **29.** Preparative VPC (10% FFAP, 205 °C) afforded **28,** >99.7% isomerically pure: IR ($CHCl_3$) 1700 (C=O); NMR ($CDCl_3$) δ 0.8–2.0 (m, 9), 0.86 (d, J = 6.2 Hz), 1.06 (d, J = 6.8 Hz), 2.6–3.3 (m, 1), 3.75 (s, 1), 3.80 (s, 5), 4.1–4.5 (m, 2). Anal. Calcd for $C_{10}H_{18}N_2O_4$: C, 52.16; H, 7.88; N, 12.16. Found: C, 52.10; H, 7.91; N, 12.01.

Preparation of a Mixture of 28 and 29. Diels–Alder reaction of *trans*-3-methyl-1,3-pentadiene and dimethyl azodicarboxylate gave dimethyl 3,4-dimethyl-3,6-dihydropyridazine-1,2-dicarboxylate in 94% yield, bp 110–112 °C (0.7 mm). Catalytic hydrogenation of the adduct over platinum gave a 95% yield of a 2:3 mixture of **29** and **28,** bp 80–92 °C (0.18 mm), which were separated by preparative VPC (FFAP, 205 °C, relative retention times, *trans*-**29** = 1.0 and *cis*-**28** = 1.14). This was a more convenient preparation than the stereospecific dimethanesulfonate procedure which was necessary for isomeric identification.

Preparation of *cis*- and *trans*-3,4- and -3,6-Dimethylhexahydropyridazines. A general procedure for hydrolysis of each isomerically pure diurethane is as follows.

One-half gram (0.002 mol) of the dimethyl 3,4-(and 3,6-)dimethyltetrahydropyridazine-1,2-dicarboxylate was added to a solution of 1 g of potassium hydroxide in 10 mL of degassed water. The mixture was allowed to reflux with vigorous stirring under a nitrogen atmosphere for 24 h. This was cooled to 0 °C, 4 mL of degassed 6 N HCl was added via syringe, and the reaction mixture was allowed to stir for 0.5 h. The reaction mixture was made basic with degassed aqueous saturated potassium carbonate and extracted three times with 25-mL portions of ether, freshly distilled under a nitrogen atmosphere and delivered via a double-ended needle. Each extract was transferred via a double-ended needle to a pressure equalizing funnel, containing

$MgSO_4$ in a small filter thimble, attached to the top of a distillation head under a slow stream of nitrogen. After the ether solvent was removed by distillation, the remaining oil was distilled on a vacuum line (10^{-4} Torr). The clear colorless hydrazo distillate was distilled into an NMR tube on the vacuum line and diluted with 0.4–0.5 mL of degassed benzene-d_6, which had been purified by preparative VPC (β,β-ODP). The NMR tube was sealed and removed.

***cis*-3,6-Dimethylhexahydropyridazine:** NMR (C_6D_6) δ 1.0 (d, 6, J = 6.7 Hz), 1.15–1.45 (m, 4), 2.30–2.95 (m, 4).

***trans*-3,6-Dimethylhexahydropyridazine:** NMR (C_6D_6) δ 0.85 (d, 6, J = 6.7 Hz), 1.0–1.8 (m, 4), 2.2–2.9 (m, 4).

***cis*-3,4-Dimethylhexahydropyridazine:** NMR (C_6D_6) δ 0.7–1.8 (m, 9), 0.76 (d, J = 6.6 Hz), 0.83 (d, J = 6.8 Hz), 2.8–3.3 (m, 5).

***trans*-3,4-Dimethylhexahydropyridazine:** NMR (C_6D_6) δ 0.6–1.6 (m, 9), 0.85 (d, J = 6.5 Hz), 1.8–2.2 (m, 1), 2.5–3.0 (m, 4).

Preparation of *cis*- and *trans*-3,4- and -3,6-Dimethyl-3,4,5,6-tetrahydropyridazines. In general, for oxidation, a solution of each dimethylhexahydropyridazine in benzene-d_6 was allowed to stand in the dark under a positive pressure of oxygen (Matheson Gas Products) for several hours. The oxidation reaction was monitored by NMR.

***cis*-3,6-Dimethyl-3,4,5,6-tetrahydropyridazine (11).** The oxidation of the *cis*-3,6-hydrazo compound **17** to the *cis*-3,6-azo compound **11** was complete in 30 h, affording a 10:1 mixture of *cis*-3,6-dimethyl-3,4,5,6-tetrahydropyridazine (**11**) and the corresponding hydrazone **37.** Azo-**11:** UV max (C_6D_6) 385 nm; NMR (C_6D_6) δ 0.41–1.5 (m, 4), 1.55 (d, 6, J = 6.8 Hz), 2.15–2.75 (m, 2).

Hydrazone **37:** NMR (C_6D_6) δ 0.78 (d, 3, J = 6.2 Hz), 1.0–1.9 (m, 8), 1.75 (s), 5.15 (br s, 1).

***trans*-3,6-Dimethyl-3,4,5,6-tetrahydropyridazines (12).** The oxidation of *trans*-3,6-hydrazo compound **18** to *trans*-3,6-azo compound **12** was complete in 56 h, affording a 5:1 mixture of *trans*-3,6-dimethyl-3,4,5,6-tetrahydropyridazines (**12**) and hydrazone **37.** Azo **12:** UV max (C_6D_6) 383 nm; NMR (C_6D_6) δ 0.5–1.5 (m, 10), 0.78 (d, J = 6.5 Hz), 1.33 (d, J = 7.0 Hz), 2.85–3.5 (m, 2).

***cis*-3,4-Dimethyl-3,4,5,6-tetrahydropyridazine (19).** The oxidation of *cis*-3,4-hydrazo compound **30** to *cis*-3,4-azo compound **19** was complete in 25 h, affording a 3:1 mixture of *cis*-3,4-dimethyl-3,4,5,6-tetrahydropyridazine (**19**) and the corresponding hydrazone, *cis*-3,4-dimethyl-2,3,4,5-tetrahydropyridazine (**38**). Azo-**19:** NMR (C_6D_6) δ 0.47 (d, 3, J = 6.8 Hz), 0.65–1.8 (m, 6), 1.44 (d, J = 7 Hz), 2.9–3.6 (m, 3). Hydrazone **38** was purified by preparative VPC (Pennwalt, 180 °C): NMR (C_6D_6) δ 0.5–3.1 (m, 10), 0.61 (d, J = 6.8 Hz), 0.75 (d, J = 6.8 Hz), 6.65 (m, 1).

***trans*-3,4-Dimethyl-3,4,5,6-tetrahydropyridazine (20).** The oxidation of *trans*-3,4-hydrazo compound **31** to *trans*-3,4-azo compound **20** was complete in 24 h, affording a 1:1 mixture of *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazine (**20**) and the corresponding hydrazone, *trans*-3,4-dimethyl-2,3,4,5-tetrahydropyridazine (**39**).

Azo-**20:** NMR (C_6D_6) δ 0.45–2.6 (m, 11), 0.61 (d, J = 6.0 Hz), 0.73 (d, J = 6.3 Hz), 6.61 (m, 1). Hydrazone **39** was purified by preparative VPC (Pennwalt, 180 °C): NMR (C_6D_6) δ 0.45–2.6 (m, 11), 0.60 (d, J = 6.0 Hz), 0.73 (d, J = 6.3 Hz), 6.6 (m, 1).

Thermal Reactions. The pyrolyses were carried out in a 2.8 × 30 cm cylindrical Pyrex tube, with a 0.6 × 3 cm injector port with serum cap, mounted in a Hoskins type FD 303A tube furnace. The other end of the tube was connected via a 6-mm bore stopcock (A) to a high vacuum line equipped with two liquid nitrogen cooled U-shaped traps plus a small receiving tube. The temperature was measured by a thermometer inserted into the furnace or an iron-constant thermocouple connected to a potentiometer. Before pyrolysis the tube was evacuated and stopcock A was closed. In a typical run, 10 μL of the solution (~10% azo in C_6D_6) was injected through the serum cap via a gas-tight syringe. After pyrolyses times of 5 to 30 s, stopcock A was opened and the pyrolysate was collected in the liquid nitrogen cooled traps. The hydrocarbon contents of the traps were transferred to the receiving tube which was sealed with a torch and removed for analysis.

The pyrolysate tube was cooled to 77 K and opened and the contents diluted with 20 μL of toluene. The products were analyzed immediately by analytical VPC (DBT and ODPN, 25 °C). Assignment of the product peaks was carried out by coinjection techniques using authentic samples. Relative retention times are as follows: (DBT, 25 °C) ethylene (0.101), propylene (0.123), *trans*-2-butene (0.211), *cis*-2-butene (0.233), *trans*-1,2-dimethylcyclobutane (0.650), 1-hexene (0.944), *cis*-1,2-dimethylcyclobutane (1.00); (ODPM, 25 °C) ethylene (0.55), *cis*- and *trans*-2-butenes (0.69), *trans*-1,2-dimethylcyclobutane (0.82), 3-methyl-1-pentene (0.90), *cis*-1,2-dimethylcyclobutanes (1.00). Each of the four azo isomers was synthesized four different times. Each sample was pyrolyzed at least three times. Analytical VPC analysis was carried out at least twice on each run.

Controls. (a) The hydrazones **37–39** were shown not to give any of the azo decomposition hydrocarbon products under identical pyrolysis conditions. (b) The products, 1,2-dimethylcyclobutanes and 2-butenes, were shown to be stable to isomerization under the pyrolysis conditions. (c) The ratio of labile azo compound to internal standard ethyl ether in benzene-d_6 was determined by NMR. After pyrolysis, the ratio of hydrocarbon products/ethyl ether afforded a rough estimate of mass balance. The remaining labile azo compound rearranged irreversibly to the corresponding hydrazone. Pressure effects (135–320 Torr) were checked by adding *n*-octane or *n*-pentane to the pyrolysis tube before the azo compound in benzene-d_6. None were found. Surface effects were checked by repeating all the pyrolyses with the tube filled with glass chips. None were found.

References and Notes

(1) Acknowledgment is made to E. I. DuPont de Nemours and Co. for a DuPont Young Faculty Grant and to the National Science Foundation (CHE75-06776) for their generous support.

(2) For a preliminary report see P. B. Dervan and T. Uyehara, *J. Am. Chem. Soc.*, **98**, 1262 (1976).

(3) Alfred P. Sloan Research Fellow, 1977–1979; Camille and Henry Dreyfus Teacher-Scholar, 1978.

(4) For example, see (a) P. D. Bartlett *Q. Rev. Chem. Soc.*, **24**, 473 (1970); P. D. Bartlett, *Science*, **159**, 833 (1968); (b) L. Salem and C. Rowland, *Angew. Chem.*, 11, 92 (1972); (c) R. G. Bergman in "Free Radicals", J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, Chapter 5; (d) G. Jones, II, *J. Chem. Educ.*, **51**, 175 (1974); (e) J. A. Berson, *Annu. Rev. Phys. Chem.*, **28**, 111 (1977).

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