modifications to the sensitivity to steric effects only for important changes in leaving group ability.

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(12) According to theoretical predictions,[2,3] the introduction of an electron-withdrawing substituent in the nucleophile of an S_N2 transition state will shorten the reacting bond which is nearer the substituent (the C–N bond). In the pyridine series with substituents of very different electronic character (alkyl, NH_2, CN), all compounds fall on one straight line (Figure 2) within the limits of experimental error. Thus these effects cancel out even when leaving groups as different as iodide and fluorosulfonate are compared.

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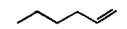
Thermal Decomposition of *cis*- and *trans*-3,4- and -3,6-Dimethyl-3,4,5,6-tetrahydropyridazines. Evidence against the Hot Diradical Postulate for Azo Decompositions

Sir:

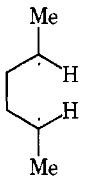
Tetramethylene diradicals are the hypothetical reactive intermediates postulated to intervene in the dimerization of olefins and the thermal cleavage of cyclobutanes.[1] Experimental efforts using stereochemical probes have been directed toward generating these reactive intermediates from different appropriately substituted precursors (olefins,[2] cyclobutanes,[3] azo compounds,[4] diazenes,[5] ketones,[6] and sulfolanes[7]) in order to characterize their behavior. Unfortunately differences in substitution, temperature, and reaction conditions have made direct comparisons of product distributions difficult.

An important 1,4-diradical with secondary radical centers is 2,5-hexanediyl (**1**),[3,6b,c,8,9] the hypothetical reactive intermediate formed by thermal cleavage of the most substituted bond in *cis*- and *trans*-1,2-dimethylcyclobutanes (studied in the gas phase at 425 ± 25° by Gerberich and Walters in 1961[3a]). Although *cis*-3,6-dimethyl-3,4,5,6-tetrahydropyridazine (**2**) has been in the literature for over a decade,[10] no successful decomposition of this pivotal azo compound for the study of **1** has been reported, nor has a synthesis of the corresponding trans isomer **3** appeared, apparently frustrated by the notoriously facile irreversible azo to hydrazone tautomerization associated with azo compounds that have enolizable hydrogens.[4b,10,11]

Table I. Percent Yields[a]

Reactant	Conditions	2 			
cis-**2**	*b*	74.7	8.5	16.3	0.5
	c	72.9	9.7	16.3	1.1
trans-**3**	*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 **2** and **3** were 50 and 80% at 306° and 439°, respectively. VPC analysis using 20 ft. × 1/8 in. 10% dibutyl tetrachlorophthalate; flame ionization detector. [b] Chamber pyrolysis (30 s at 306 ± 2°, est pressure >25 mm). [c] Chamber pyrolysis (5 s at 439 ± 2°, est pressure >31 mm).



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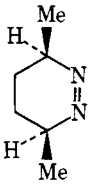

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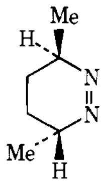
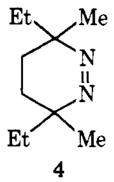


3

We now wish to report the successful stereospecific synthesis[12] and thermal decomposition in the gas phase (306–439°) of both *cis*- and *trans*-3,6-dimethyl-3,4,5,6-tetrahydropyridazines (**2** and **3**, respectively). Conditions and results of the pyrolyses are listed in Table I.[18]

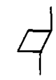
Examination of the 1,2-dimethylcyclobutane product ratios from the cis- and trans azo decompositions (**2** and **3**, respectively) reveals that, although overall retention is preserved, the loss of stereochemistry in the closure products is relatively high (at 306°, retention/inversion (r/i) ratios are 1.9 and 2.2 from **2** and **3**, respectively) compared to the more highly substituted cyclic azo system with tertiary radical centers reported by Bartlett and Porter (at 148°, r/i ratios are ≥49 from both *meso*-, and *dl*-azo-**4**).[4a] If 1,4-diradicals with secondary centers intervene in the decomposition of **2** and **3**, the data indicate that carbon–carbon bond rotation is *competitive* with cleavage and closure. Thus, the intermediates formed from azo compounds **2** and **3** are similar in behavior to those from the thermal decomposition of *cis*- and *trans*-1,2-dimethylcyclobutanes.[3a]



4

Stephenson and Brauman[8] attempted to explain the high stereospecificity observed in the cyclic azo-**4** decomposition (as compared to the less stereospecific thermal reactions of 1,2-dimethylcyclobutanes) by directing attention to the *mode of generation* of the intermediates in the two cases. They explained the higher stereospecificites observed from **4** by suggesting that vibrationally "hot" 1,4-diradicals are

Table II. Percent Yields[a]

Reactant	Conditions				
cis-5	*b*	11.2	69.5	4.7	14.6
	c	11.4	64.4	8.2	16.0
trans-6	*b*	69.7	4.3	23.4	2.6
	c	68.7	5.2	23.2	2.9

[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°, respectively. VPC analysis using 20 ft. × 1/8 in. 10% dibutyl tetrachlorophthalate; flame ionization detector. [b] Chamber pyrolysis (30 s at 306 ± 2°, est pressure >25 mm). [c] Chamber pyrolysis (5 s at 439 ± 2°, est pressure >31 mm).

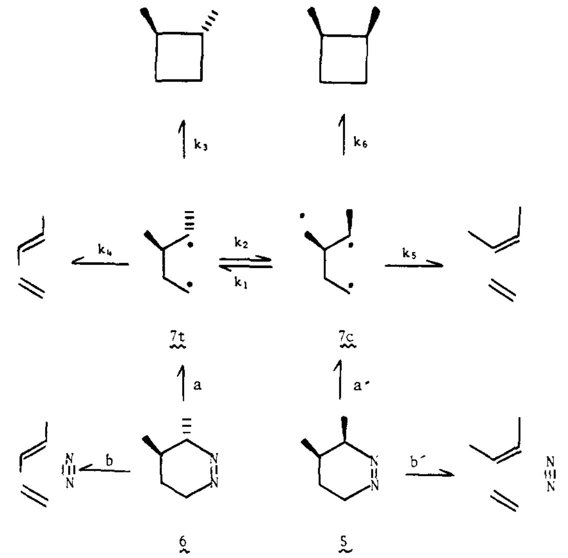
formed from azo precursors whereas thermally equilibrated 1,4-diradicals are generated in the cyclobutane pyrolyses. The work described here demonstrates that when the thermal reactions of cyclic azo compounds and cyclobutanes of similar substitution are compared at the same temperature, the stereospecificities are similar, and therefore the need for the "hot" diradical postulate disappears.[19] Moreover our results are consistent with the view that entropy effects and rotational barriers due to differences in substitution at the radical centers are responsible for the differences in stereospecificities (i.e., stereospecificity increases as substitution at the radical center increases).[3d,f,6b] These results emphasize the important point that the only valid comparison between thermally generated high energy species from difference precursors (and hence different points on an energy surface) must involve *structures of similar substitution at the same temperature.*

The thermal decomposition of a differently substituted azo precursor provides information on the cleavage stereochemistry in the six-membered cyclic azo system. In a series of elegant studies, Berson and co-workers have shown kinetic and stereochemical evidence that six-membered cyclic azo compounds with a π or bent σ backbone bond undergo what appears to be concerted (2 + 2 + 2) cycloreversions with the degree of concert diminishing as the backbone bond orbital acquires more σ character.[11c] A question that remains unanswered is whether some degree of concert is left if the backbone bond were pure σ. We report here the stereospecific synthesis and thermal decomposition in the gas phase (306–439°) of *cis*- and *trans*-3,4-dimethyl-3,4,5,6-tetrahydropyridazines (**5** and **6**, respectively).[20,21] These experiments allow us to test whether fragmentation and ring-closure products in six-membered cyclic azo thermal reactions arise exclusively from a common set of azo generated 1,4-diradicals (**7t** and **7c**) (paths a, a′ in Scheme I) or whether a direct pathway to fragmentation products is also occurring (path b, b′ in Scheme I). Conditions and results of the pyrolyses are listed in Table II.[22]

Examination of the data reveals that the ratio of *trans*-2-butene/*trans*-1,2-dimethylcyclobutane is higher from the trans azo precursor than from the cis azo precursor (at 439°, 3.0 vs. 1.4). Similarly, the ratio of *cis*-2-butene/*cis*-1,2-dimethylcyclobutane is higher from the cis azo precursor than from the trans azo precursor (at 439°, 4.0 vs. 1.8). Thus there is an *extra component of stereospecific cleavage of retained* stereochemistry from each azo compound.

The crossover cleavage/closure product ratios from the cis and trans azo decompositions afford directly the azo-generated 1,4-diradical *k*(cleavage)/*k*(closure) ratios (k_4/k_3 = 1.4, k_5/k_6 = 1.8). The *k*(cleavage)/*k*(closure) ratios and the cis/trans ratios of cyclobutane products observed from each azo isomer provide *k*(closure)/*k*(rotation) ratios (k_3/k_2 = 1.9, k_6/k_1 = 0.7) from a steady-state analysis of the proposed diradical scheme. From these relative rates of rotation, cleavage, and closure for the two isomeric azo-generated 1,4-diradicals the calculated *trans*/*cis*-2-butene and *cis*/*trans*-2-butene ratios from **7t** (from *trans* -azo-**6**) and **7c** (from *cis*-azo-**5**) are 86/14 and 72/28, respectively. They compare favorably with 88/12 and 68/32 from *trans*- and *cis*-1,2-dimethylcyclobutanes reported at 440° by Gerberich and Walters.[3a] The observed 2-butene ratios (Table II) are consistent with a direct cleavage component (path b = 37%, b′ = 35%) superimposed on a 1,4-diradical intermediate (path a = 63%, a′ = 65%)[23] remarkably similar in behavior to that generated under the same conditions (gas phase, 440°) in the thermal decomposition of *cis*- and *trans*-1,2-dimethylcyclobutanes. It is suggestive that this system represents the point where the 1,4-diradical and the (2 + 2 + 2) cycloreversion are now competitive and that the last traces of concert do indeed survive in pure σ cyclic azo decompositions.[24]

Scheme I



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(12) Diels–Alder addition[13] of *trans,trans*- and *cis,trans*-hexa-2,4-diene to dimethyl azodicarboxylate, followed by hydrogenation, afforded the *cis*- and *trans*-diurethane precursors[14] (99 and 97% isomerically pure[16]).

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(14) 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 were distilled on a vacuum line (10^{-4} Torr). Oxidation of the pure hydrazines in benzene-d_6 to the corresponding azo compounds was accomplished by treatment with oxygen and monitored by NMR.[15] For pyrolysis, these solutions were injected into an evacuated Pyrex chamber (preheated to 306 and 439°) and the products were collected in a trap at −196°. The product ratios were determined by electronically integrated analytical vapor phase chromatography (VPC) analysis.

(15) We thank Dr. E. Petrillo, Jr.,[11c] for helpful suggestions during the course of this work.

(16) Treatment of the diurethanes with $LiAlH_4$ afforded the corresponding tetramethylhexahydropyridazines[17] which were analyzed by analytical vapor phase chromatography.

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(18) Surface effects were checked. None was found. Control experiments show that the hydrocarbon products are stable under the pyrolysis conditions. Hydrazone by-product was shown not to give cyclobutane or olefin products under the pyrolysis conditions.

(19) The azo generated diradical is either not formed "hot" or if "hot" the excess vibrational energy has no substantial chemical consequences.

(20) Hydroboration of 3-methyl-*cis*- and -*trans*-1,3-pentadiene followed by oxidation afforded *erythro*- and *threo*-3-methylpentane-1,4-diol. Reaction of the corresponding erythro and threo diol dimethanesulfonates with dimethylhydrazo-1,2-dicarboxylate and sodium hydride afforded dimethyl *trans*- and -*cis*-3,4-dimethyltetrahydropyridazine-1,2-dicarboxylates.[14] The cis and trans diurethanes were further separated by preparative vapor phase chromatography (≥99.5% isomeric purities). These diurethanes gave satisfactory C,H analysis and spectral data.

(21) These azo compounds suffered facile irreversible azo to hydrazone tautomerization in the presence of trace amounts of acid, base, solvents, and light.

(22) Product ratios were insensitive to changes in surface area and pressure (30–500 mm). Decomposition in benzene (sealed tubes) at 306° gave similar results. Control experiments show that the hydrocarbon products are stable under the pyrolysis conditions. Hydrazone by-product was shown not to give cyclobutane or olefin products under the pyrolysis conditions.

(23) From azo-**6** *trans/cis*-2-butene 68.6/5.2 (observed) = 36.6 (direct) + 32.0/5.2 (diradical) and from azo-**5** *cis/trans*-2-butene 64.0/11.3 (observed) = 35.4 (direct) + 28.6/11.3 (diradical).

(24) The hot diradical postulate proposes the vibrationally hot 1,4-diradicals have $k(\text{rotation}) \ll k(\text{closure}) \sim k(\text{cleavage})$ from $A(\text{rotation}) \ll A(\text{closure}) \sim A(\text{cleavage})$.[8,3a] An attempt to fit the azo data to the hot diradical postulate would require $A(\text{rotation}) \sim A(\text{closure}) \ll A(\text{cleavage})$.

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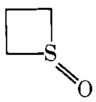
Sulfine[1]

Sir:

While a wide variety of substituted sulfines are known and are generally described as stable substances,[2] the parent compound, CH_2SO, has thus far eluded synthesis.[2a,3] We now wish to report the facile generation of sulfine (thioformaldehyde *S*-oxide) by flash vacuum pyrolysis (FVP) of a number of readily available precursors. We also report herein the structure of this intriguing molecule as determined by microwave spectroscopy.

In view of the demonstrated generation of other elusive "heteroolefinic" species by pyrolysis or photolysis of various four-membered rings,[4] heterocyclobutanes **1** and **2** seemed to be likely sulfine precursors. Indeed, initial study of the FVP of thietane *S*-oxide (**1**)[5] and 1,3-dithietane 1-oxide (**2**)[6] (utilizing a pyrolysis system[7] connected directly to the source of a mass spectrometer) suggested that both compounds decomposed cleanly to sulfine in the gas phase beginning at temperatures of ca. 600° and 300°, respectively. Definitive evidence for the formation of sulfine from **1** and **2** under FVP conditions was obtained by following the decomposition of **1** and **2** by microwave spectroscopy. Thus, when **2** at its vapor pressure of 25μ was evaporated through a pyrolysis tube into a microwave absorption cell, generation of sulfine was detected first at a pyrolysis temperature of 300 °C and was complete above 500° at which temperature the spectrum of **2**[6] had been replaced by the spectra of thioformaldehyde[8] and sulfine.



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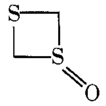


2

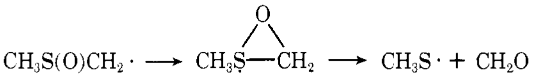
A number of other possible precursors of sulfine were examined using FVP-mass spectrometry and FVP-microwave spectroscopy techniques. Pyrolysis of 1,3,5-trithiane has been shown to generate thioformaldehyde.[8] We find that sulfine is produced, albeit inefficiently, on FVP of 1,3,5-trithiane 1-oxide.[9] The pyrolysis of Me_2SO is suggested to involve a chain decomposition with sulfine as one intermediate (eq 1–3).[10]

$$CH_3S(O)CH_3 \xrightarrow{\Delta} CH_3SO\cdot + CH_3\cdot \quad (1)$$

$$CH_3S(O)CH_3 + CH_3\cdot \longrightarrow CH_4 + CH_3S(O)CH_2\cdot \quad (2)$$

$$\underset{\mathbf{3}}{CH_3S(O)CH_2\cdot} \longrightarrow CH_3\cdot + CH_2SO \quad (3)$$

In our hands FVP of Me_2SO at 650° did in fact generate sulfine, though not as efficiently as did FVP of **2**. Since Gollnick[11] has postulated that radical **3**, when generated by photolysis of neat Me_2SO, undergoes an alternative mode of decomposition than that indicated by eq 3, namely, rearrangement followed by fragmentation (eq 4), it seemed desirable to provide additional support for the thermal radical fragmentation process of eq 3. Iodomethylmethyl sulfoxide (**4**)[12] appeared to be a suitable precursor to radical **3**. FVP of **4** at 350° did indeed generate sulfine together with methyl iodide (both rather inefficiently), perhaps via the sequence of reactions indicated in eq 5–7.



$$CH_3S(O)CH_2\cdot \longrightarrow CH_3\overset{O}{S\!-\!\!-}CH_2 \longrightarrow CH_3S\cdot + CH_2O \quad (4)$$

$$CH_3S(O)CH_2I\ (\mathbf{4}) \xrightarrow{\Delta} CH_3S(O)CH_2\cdot + I\cdot \quad (5)$$

$$CH_3S(O)CH_2\cdot \longrightarrow CH_2SO + CH_3\cdot \quad (6)$$

$$CH_3S(O)CH_2I + CH_3\cdot \longrightarrow CH_3S(O)CH_2\cdot + CH_3I \quad (7)$$

Base induced dehydrochlorination of alkane- or arylalkanesulfinyl chlorides has been widely used to generate substituted sulfines,[2a,c,d,g] although the reaction reportedly fails with methanesulfinyl chloride.[2a,3] We find that FVP of methanesulfinyl chloride at 600° affords HCl and sulfine. In examining FVP routes to sulfine homologues, we find that FVP of ethanesulfinyl chloride and 2-propanesulfinyl