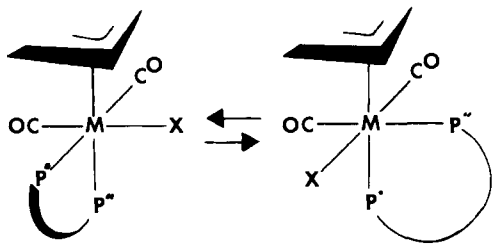
rangement that is fully consistent with the dynamic NMR spectra is shown below.



This mechanism can be described as a trigonal twist, in which the rotation of the triangular face formed by the halogen and the two phosphorus atoms relative to the face formed by the allyl and two carbonyl groups.[14] The chirality at the metal center may be designated (*S*) or (*R*) according to the octahedral sequence and chirality rules set forth by Cahn, Ingold, and Prelog.[15] Using this terminology, the inversion of chirality produced by the rearrangement can be described as an interconversion of (*S*)- and (*R*)-(η^3-C_3H_5)M(CO)$_2$(P-P)X. This process is consistent with the averaged spectra which show that the methylene protons of diphos remain nonequivalent, the methylene protons of dppm remain nonequivalent, the terminal allyl protons are not equally coupled to both phosphorus nuclei, but the vinylic protons of dppe are averaged. The carbonyl carbon nuclei show unequal coupling to the phosphorus nuclei as well, indicating that the relationship of the allyl to the carbonyls about that triangular face is retained. Therefore, even though enantiomerization occurs at the metal center in this case,[16] the spatial relationships within the X-P′-P″ unit are maintained. That is, even though the structure is nonrigid, the same side of the chelating phosphine remains oriented toward the halogen.

This implies that in the chiral structure formed with arphos, this twist process will interconvert certain pairs of isomers, but not invert the chirality of the X-As-P unit. A formal description of this process does not have an analogue in structures based on tetrahedra. In a tetrahedron on (*R*) or (*S*) designation can be assigned to each of the triangular faces; however, the specification of the chirality of one face is sufficient to completely describe the configuration about a tetrahedron. In sufficiently complex octahedral structures, the chirality rules break down;[16] nevertheless, the chirality associated with each of the triangular faces can still be specified. That is, if As replaces P′ in the diagram, an (*R*)-AsPX configuration should be retained during the rearrangement, whereas (*R*)-X(allyl)CO is inverted to (*S*)-X(allyl)CO. Thus the isomerization observed for the arphos derivative might be described as an epimerization.

The allyl-metal-dicarbonyl fragment is prochiral and since the As-P-X unit should retain its chirality, the carbonyls and the termini of the allyl should be diastereotopic. Thus, one observes that the terminal protons of the allyl are not equivalent in the averaged spectra of the arphos derivative.[17] The essential feature of this discussion is that, despite the nonrigidity of the molecule, certain elements of chirality are retained during the rearrangements; therefore, asymmetric induction can be anticipated in the reactions of the allyl moiety. A detailed discussion of the consequences of the chirality retention on the NMR spectra and the stereoselectivity of reactions of these complexes will be forthcoming.

Acknowledgments. This research was supported by a grant from the National Science Foundation (CHE76-10762). NMR spectra for ^{1}H and ^{13}C were obtained at 270 MHz and 67.9 MHz at the Southern New England High Field NMR Facility (NIH No. 1-P07-PR00798) and 36.5-MHz ^{31}P spectra through the courtesy of Dr. Ian Armitage.

Supplementary Material Available: Important bond distances (Table I) and bond angles (Table II) (3 pages). Ordering information is given on any current masthead page.

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(7) Space group = $P2_1/n$; unit cell: a = 11.442 (1), b = 18.004 (13), c = 14.504 (8) Å; β = 106.54 (3)°; Z = 4.
(8) Intensity data were collected on a Picker FACS-1 automatic diffractometer, operating in the θ–2 θ scan mode with K_α = 0.7093. The number of reflections with $F^2 > 3\sigma(F^2)$ used was 2006 and the reflections were collected in the scan range of 0–50. The structure was solved by heavy atom methods. Full-matrix least-squares refinement converged to the conventional discrepancy indices R = 0.060 and R_w = 0.057.
(9) These complexes can be viewed as octahedral if the η^3-allyl group is assumed to occupy only one coordination position.
(10) An unweighted least-squares plane including the atoms Cl, P1, C2, and C1 conforms to the equation $-7.611x + -13.037y + 5.123z + 1.8600 = 0$. The distances in Å of these atoms to the plane they describe are as follows: Cl = 0.079, P1 = −0.077, C1 = −0.108, and C2 = 0.105. The distance of the Mo atom from this plane is 0.237 Å.
(11) The abbreviations for the ligands are: bis(diphenylphosphino)ethane = diphos; *cis*-bis(diphenylphosphino)ethylene = dppe; bis(diphenylphosphino)methane = dppm, and 1-(diphenylphosphino)-2-(diphenylarsino) ethane = arphos.
(12) Similar infrared and limiting low-temperature ^{1}H, ^{13}C, and ^{31}P NMR spectra indicate that all compounds are isostructural.
(13) For example, the diphos–iodide complex shows an AA′BB′X pattern at 50 °C with chemical shifts of δ 1.82, 3.80, and 4.05 for the anti, syn, and central protons, respectively. At −100 °C resonances are observed at δ 1.33 and 1.99 for the anti, δ 3.25 and 4.46 for the syn, and δ 3.93 for the central protons. The diphos methylene protons resonate at δ 1.33, 1.99, 2.36, and 3.00 at −100 °C, and at δ 2.37 and 3.14 at 50 °C. The methylene protons of dppm resonate at δ 4.19 and 4.71 at 25 °C and do not vary significantly as the temperature is lowered in the ^{31}P decoupled spectra.
(14) These variations do not arise from conformations of the chelate rings. The similarity in the spectral properties of the diphos, dppm, and dppe demand that the dynamic NMR spectra result from processes other than conformational interconversion within the chelate rings. Effects from flexing of the five-membered ring in diphos begin to occur below −120 °C. It has been shown previously that the λ–δ interconversion in diphos rings occur rapidly on the NMR time scale (e.g., P. R. Hoffman, J. S. Miller, C. B. Ungermann, and K. G. Caulton, *J. Am. Chem. Soc.*, **95**, 7902 (1973)).
(15) The configuration assignments shown in the drawing refer to X = iodide. Priorities of polyhapto ligands follow the recommendations of K. Stanley, and M. C. Baird, *J. Am. Chem. Soc.*, **97**, 6598 (1975). The rules for octahedral complexes are given by R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966), and the IUPAC, *J. Org. Chem.*, **35**, 2849 (1970).
(16) Enantiomerization occurs at the metal center in twist rearrangements of tris chelates (e.g., M. Pickering, B. Jurado, and C. S. Springer, *J. Am. Chem. Soc.*, **98**, 4503 (1976)). In most tris chelates studied to date the chirality is associated with the helicity of the chelate rings and is thus termed "secondary" chirality.[15] Our complexes are chiral by virtue of having four different types of substituents; hence, the chirality is "primary" and descriptors of helicity are inappropriate. The octahedral sequence rules[15] assume that the ligands of highest priority can be placed in a fac arrangement. When X = chloride, the sequence P′ > P″ > (allyl) is in a mer arrangement and therefore the chirality cannot be specified by the existing rules.
(17) The arphos–iodide exhibits resonances for the terminal protons of the allyl at δ 1.71, 1.82, 3.68, and 3.88 at 20 °C.

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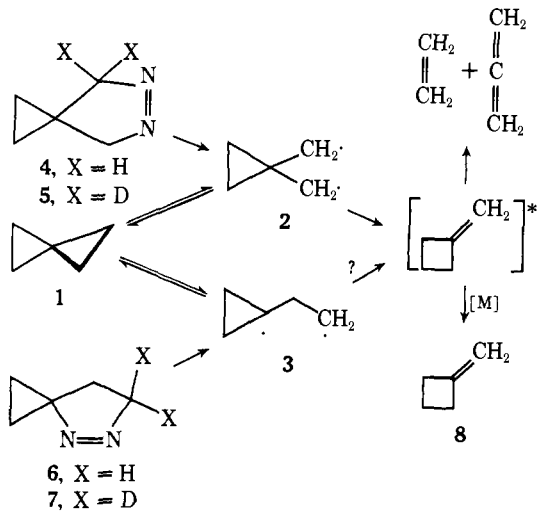
An Azo Compound Route to Spiropentane Thermolysis Intermediates. Formation of Vibrationally Excited Organic Molecules in the Thermal Decomposition of Pyrazolines, and Evidence Concerning the Distribution of Excess Energy in Reaction Products

Sir:

Questions concerning the mechanism of thermal decomposition of spiropentane (**1**; Scheme I) have for some time centered around the relative energies of cleavage of the so-

Scheme I



called "peripheral" and "radial" C–C bonds in this molecule which may lead, respectively, to diradicals **2** and **3**.[1] The spiropentane decomposition is also interesting in that, besides leading to rearrangement product methylenecyclobutane (**8**), it gives a significant and pressure-dependent amount of fragmentation products, ethylene and allene, indicating that vibrationally excited (chemically activated) methylenecyclobutane is produced and decomposes very efficiently in this reaction.[2] Despite these observations, and the fact that pyrazolines have now become routine alternative precursors to numerous other substituted trimethylene diradicals,[3] no report exists of attempts to generate **2** and **3** from appropriate cyclic azo compounds **4** and **6**.

We now wish to report the synthesis and thermal decomposition of **4** and **6** and their dideuterated analogues **5** and **7**, because (1) we believe these experiments considerably illuminate the mechanism of spiropentane decomposition by providing direct information about the chemical behavior of independently generated diradicals **2** and **3**; (2) **4** and **6** appear to be the first five-membered cyclic azo compounds which generate vibrationally excited organic molecules upon *thermal* decomposition;[4] (3) our studies have uncovered an unexpected difference in the behavior of the vibrationally excited molecules generated from **4** and **6**, and we believe this difference provides important and heretofore unavailable information concerning the disposition of vibrational energy in the fragments resulting from dissociation of complex organic molecules.

We consider first the product distribution and labeling data for symmetrical pyrazoline **4** and its deuterated analogue **5** (Tables I and II).[5] The products observed support the idea that decomposition of this molecule proceeds through an intermediate whose gross structure is the same as that of the intermediate generated in the spiropentane decomposition;[1] as is observed in other pyrazoline thermolyses,[3] ring closure predominates over rearrangement by a factor of about 99:1. Interestingly, small amounts of ethylene and allene are also observed. The label distribution in these fragmentation products rules out their exclusive formation by "direct" cleavage of two cyclopropane C–C bonds[1b,c] in diradical **2** (Scheme II); were this to happen, all the deuterium would be found in the allene. The simplest way to account for the nearly 75:25 distribution is to assume that vibrationally excited methylenecyclobutane (formed by ring expansion in **2**; Scheme II) is the source of these materials. The approximately eightfold decrease in the methylenecyclobutane/ethylene–allene ratio observed in dropping the pressure to 0.2 Torr is supportive evidence for this mechanism. This experiment also shows that the yield of spiropentane does not change with pressure, and thus (unlike **8**),

Table I. Products Formed on Pyrolysis of Pyrazolines **4** and **6**

Starting material	Conditions[a]	Run no.	Products,[b,d] % 1	8	Ethylene + Allene	Unident.
4	195 °C, 35 Torr N_2, static	1	99.00	0.98	0.02	—
		2	99.01	0.97	0.02	—
	195 °C, 0.2 Torr, static	1	99.01	0.87	0.12	—
		2	99.01	0.84	0.15	—
	341 °C, 1 atm, flow	1	97.52	2.45	0.03	—
		2	97.62	2.10	0.28	—
		3	97.60	2.14	0.26	—
	341 °C, 0.2 Torr, flow		97.60	2.37	0.03	—
	401 °C, 1 atm, flow		94.49	5.33	0.18	—
	402 °C, 0.02 Torr, flow	1	95.2	4.0	0.8	—
		2	95.8	3.4	0.8	—
		3[c]	95.4	3.9	0.7	—
6	341 °C, 1 atm, flow	1	97.23	1.13	0.15	1.49
		2	98.02	0.89	0.21	0.88
		3[c]	97.88	0.91	0.21	1.00
	341 °C, 0.2 Torr, flow	1	81.38	5.68	11.56	1.38
		2	81.22	5.64	11.75	1.39
		3[c]	81.12	5.53	11.77	1.58
		4[c]	81.30	5.61	11.66	1.43

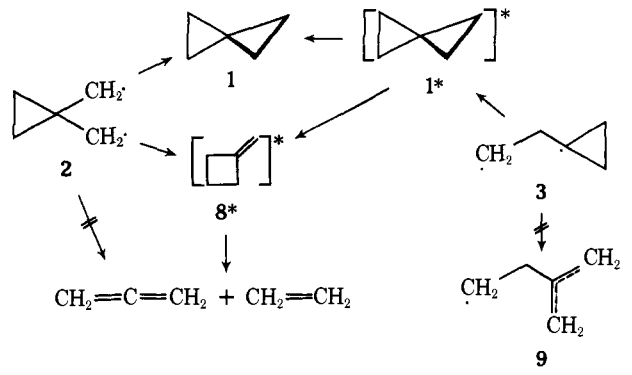
[a] Pyrolyses carried out in either a well-conditioned 200-mL quartz vessel (static system) heated by a constant-temperature oil bath or in a quartz tube (flow system) heated with a Hoskins furnace. [b] Analysis carried out by repetitive GC analysis using a Hewlett-Packard 5750 instrument coupled to an Autolabs System I computing integrator. [c] Reaction vessel packed with quartz tubes; surface/volume ratio increased by approximately a factor of 5. [d] Absolute yield of hydrocarbons measured in the following runs: 4, 341 °C, 1 atm, flow, 97%; 341 °C, 0.2 Torr, flow, 92%; **6**, 341 °C, 1 atm, flow, 86%; 341 °C, 0.2 Torr, flow, 86%. Yields measured by digital integration of VPC signals vs. internal standard, with appropriate response factor calibration.

Table II. Distribution of Istopic Label in Fragmentation Products Formed from **5** and **7**

Starting material	Conditions	Ratio[a] d_0:d_2 CH_2=C=CH_2	CH_2=CH_2
5	195 °C, 0.2 Torr (static)	24:76	71:29
	341 °C, 1 atm (flow)	27:73	76:24
	401 °C, 1 atm (flow)	42:58	58:42
7	341 °C, 1 atm (flow)	54:46	45:55

[a] Analyses carried out using coupled GC–MS system at 10.01 eV ionization voltage.

Scheme II



1 is apparently *not* generated in vibrationally excited form. The runs at higher temperatures demonstrate that at 341 °C spiropentane undergoes very slight decomposition to methylenecyclobutane, but temperatures in excess of 400 °C are required to produce any detectable secondary allene and ethylene, presumably by thermal decomposition of methylenecyclobutane.

The results for **6** are strikingly different. Once again, spiropentane is the major product of the reaction. Methylene cyclobutane is also formed, as are ethylene and allene, but in amounts significantly larger than those observed from **4**; small amounts of unidentified hydrocarbons are also detected. One possible way for the methylenecyclobutane to arise is via a second ring opening in **3** (Scheme II) leading to the "allylically stabilized diradical" **9** which has been discussed by Flowers and his co-workers.[1b,c] However, if this were the only route to fragmentation products, *all* the deuterium label in the decomposition of **7** should appear in the ethylene product. The actual observation is that the label is distributed *nearly equally* in the two fragmentation products (Table II). This suggests strongly that the ultimate source of the ethylene and allene is a compound which has spiropentane symmetry. Controls again show that no fragmentation products are formed thermally at these temperatures. That *both* vibrationally excited **1** and **8** must intervene in this reaction is confirmed by variable pressure studies (Table I)—in this case (unlike that of **4**) both the spiropentane and methylenecyclobutane yields are now pressure dependent.

Why does unsymmetrical pyrazoline **6** give rise to vibrationally excited spiropentane (**1**), but symmetrical pyrazoline **4** does not? One possible explanation for this might be found in differing heats of formation for the diradicals **2** and **3** or for the transition states leading to them. However, although there is some uncertainty in the group equivalent calculations needed to make such estimates,[6] it is difficult to make a case that these heats of formation will differ by more than a few kilocalories per mole in the two cases. A much more convincing explanation is provided by a postulate put forward by Bauer several years ago, suggesting that the distribution of vibrational energy in fragmentation reactions of the type discussed here might be determined by their decomposition mechanisms.[7]

Translated into terms applicable to azo compounds **4** and **6**, Bauer's postulate[7a] suggests the following: symmetrical compound **4** probably decomposes by simultaneous cleavage of both C–N bonds, passing through a short-lived, symmetrical transition state in which coupling of the N–N vibration with vibrational modes in the organic fragment is very poor. Thus the nascent N_2 molecule is generated initially with an N–N bond that is "stretched"—i.e., the N_2 is formed vibrationally excited, and carries off much of the excess energy of the decomposition, leaving an essentially thermalized organic fragment. Pyrazoline **6**, however, has one strong and one weak C–N bond; there is now good precedent that such azo compounds decompose by sequential C–N cleavage,[8] initially generating diazenyl (i.e., $R-N_2\cdot$) radicals. Bauer suggests[7a] that such nitrogen-containing diradical intermediates should have time to allow efficient coupling between the N–N vibration and the vibrational modes of the organic fragment; thus the N_2 will be extruded "cold", leaving most of the excess energy behind in the organic fragment. This explanation accounts very nicely for our observations, and provides strong encouragement to the search for spectroscopically observable "hot" nitrogen extruded in the thermal decomposition of *symmetrical* cyclic azo compounds.

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(3) See R. G. Bergman in "Free Radicals," Vol. 1, J. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 3, and references cited there.

(4) (a) Perhaps the most careful previous search was reported by F. H. Dorer, E. Brown, J. Do, and R. Rees, *J. Phys. Chem.,* **75,** 1640 (1971). (b) For an interesting discussion of some of the possible consequences of chemical activation in pyrazoline pyrolyses, see L. M. Stephenson and J. I. Brauman, *J. Am. Chem. Soc.,* **93,** 1988 (1971). (c) Hot hydrocarbons have been detected in pyrazoline *photochemical* decompositions; see, for example, F. T. Thomas, C. I. Sutin, and C. Steel, *J. Am. Chem. Soc.,* **89,** 5107 (1967); F. H. Dorer, *J. Phys. Chem.,* **73,** 3109 (1959); **74,** 1142 (1970). (d) For evidence that hot *tert*-butyl radicals are generated in the decomposition of azo-*tert*-butane, see D. F. McMillen, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.,* **94,** 4403 (1972).

(5) Compounds **4–7** were prepared by allowing methylenecyclopropane and diazomethane (or diazomethane-d_2) to stand in diethyl either solution at ca. 3 °C for 2 weeks. The mixture of two azo compounds was obtained in 90% yield; the ratio of **4:6** was 45:55. The isomers were separated by preparative VPC on a 20 ft by ¼ in. QF1 glass column and characterized by standard spectral and analytical techniques.

(6) Azo compound heats of formation are discussed by P. S. Engel, J. L. Wood, J. A. Sweet, and J. L. Margrave, *J. Am. Chem. Soc.,* **96,** 2381 (1974). The activation energy for thermal decomposition of **4** in solution is 39.9 ± 1.5 kcal/mol at 160 °C; we estimate that E_a for decomposition of **6** is 3–4 kcal/mol higher than that of **4**.

(7) (a) S. H. Bauer, *J. Am. Chem. Soc.,* **91,** 3688 (1969). For a more general discussion of the factors influencing energy disposition in elementary reactions, see (b) J. C. Polanyi, *Acc. Chem. Res.,* **5,** 161 (1972).

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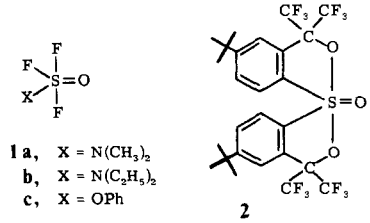
The Acid Catalyzed Fragmentation of a Spirobicyclicsulfurane Oxide: Sulfone Formation as a Driving Force for Reaction[1]

Sir:

Sulfurane oxide intermediates or transition states have often been proposed in nucleophilic substitution reactions on sulfur.[2] The preparations of sulfur oxytetrafluoride and a number of other halogen substituted sulfurane oxides, including **1a–c**, have also been reported.[3] Sulfurane oxide **2**, the only reported ketal analogue of a sulfone,[4] was found to be inert toward aqueous acid or base.



1a, X = $N(CH_3)_2$
b, X = $N(C_2H_5)_2$
c, X = OPh

2

We report here the first example of a new type of fragmentation reaction which involves the smooth transformation of spirobicyclicsulfurane oxide **3** to sulfone-ene-ol **4**. The formation of the very stable, neutral, sulfone function of **4** provides a strong driving force for this reaction. The energy of the S=O