

These findings exclude the possibility of external *t*-butoxy radical combination for the following reasons. Even if reaction 7 were not fast, the subsequent reactions 1, 3, and 7' constitute a chain in which 8 cumyloxy radicals are made for each *t*-butoxy radical.<sup>3,13a</sup> Therefore an upper limit for the production of DBP by external combination (reaction 2) is only  $100(1/9)^2 = 1.3\%$ , the remainder being dicumyl peroxide and *t*-butylcumyl peroxide. Because reaction 7 is fast,<sup>15</sup> it is unlikely that any of the DBP results from external combination under these conditions. The failure of excess diphenylpicrylhydrazyl to prevent DBP formation further substantiates this conclusion.

We conclude from these experiments that all of the di-*t*-butyl peroxide obtained from DBPO is a product of the cage reaction (6a). The discovery of such facile cage recombination of *t*-butoxy radicals separated by 2 molecules of carbon dioxide has important implications in other reactions producing more intimate pairs of alkoxy radicals (e.g., eq. 5).

The results of investigations of reaction 5 will be reported later.<sup>3b,13a,b</sup>

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### Thermal Decomposition of *cis*- and *trans*-3,5-Dimethyl-1-pyrazoline

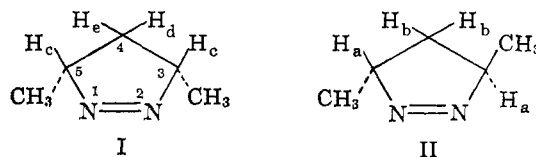
Sir:

Previously we provided kinetic data for 1,3-diradicals as intermediates in the thermal decomposition of 1-pyrazolines.<sup>1</sup> We wish to report further observations on these diradicals.

Similarly *dl*-2,4-dibromopentane<sup>2</sup> gave *trans*-3,5-dimethylpyrazolidine, b.p. 69–70° (40 mm.);  $n_D^{25}$  1.4580; 57% yield. The pyrazolidines were oxidized<sup>1</sup> to *cis*-3,5-dimethyl-1-pyrazoline (I, b.p. 60–61° (40 mm.), 138–139° (700 mm.);  $n_D^{25}$  1.4285) and *trans*-3,5-dimethyl-1-pyrazoline (II, b.p. 60–61° (40 mm.);  $n_D^{25}$  1.4347), respectively. Hydrogenation of 3,5-dimethyl-2-pyrazoline over Adams catalyst (70° in methanol) also produces *cis*-3,5-dimethylpyrazolidine.

That the pyrazoline from *dl*-2,4-dibromopentane has the *trans* configuration was demonstrated by the equivalence of the methylene protons on C-4. A 100-Mc. n.m.r. spectrum of II displayed the methinyl protons H<sub>a</sub> as a sextet at  $\tau$  5.43. The methylene protons H<sub>b</sub> appear as a triplet at  $\tau$  8.73 ( $J = 8.5$  c.p.s.) and the methyl protons as a doublet at  $\tau$  8.71 ( $J = 7.0$  c.p.s.). The *cis* isomer I displayed methinyl protons H<sub>c</sub> as a sextet at  $\tau$  5.80 and the methyl protons as a doublet at  $\tau$  8.46 ( $J = 7.0$  c.p.s.). The C-4 methylene protons form an AB quartet ( $\delta = 164$  c.p.s. at 100 Mc. and 96 c.p.s. at 60 Mc.,  $|J_{e,d}| = 12.5$  c.p.s.) centered at  $\tau$  8.72. Each line was further split into a triplet by the adjacent methinyl protons ( $J = 8.5$  c.p.s.).<sup>3</sup>

The gas-phase decomposition proceeds by first-order kinetics at 220° to produce the products shown in Table I. The pyrazolines were degassed and sealed in ampoules which were heated to 220°, and the ampoules



were broken directly in the helium stream of a gas chromatograph using a heated bulb crusher. The pressure in the bulbs approximated 1 atm. on completion of reaction. The reaction products were identified by retention times on two columns (a 20-ft. silver nitrate-propylene glycol and an 8-ft. silica gel column) by peak enrichment from authentic samples<sup>4</sup> and by mass spectrometry.

The results indicate that I decomposes through a different diradical species than II, and that I reacts

Table I. Products of the Thermal Decomposition of I and II

Pyrazolines	1,2-Dimethylcyclopropane <sup>a</sup>		2-Pentene	
	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>
I ( <i>cis</i> )	33.2 ± 0.6 <sup>b</sup>	66.1 ± 0.6	0.0	0.68 ± 0.08
II ( <i>trans</i> )	72.6 ± 0.4	25.4 ± 0.6	0.92 ± 0.11	1.08 ± 0.17

<sup>a</sup> All products and reactants were checked for isomerization under the reaction conditions. <sup>b</sup> Average deviation as a result of six runs.

*cis*-3,5-Dimethylpyrazolidine was prepared by refluxing for 2 hr. 50 g. of *meso*-2,4-dibromopentane<sup>2</sup> in a solution of hydrazine in ethanol. On cooling, the precipitated hydrazine hydrobromide was separated and potassium hydroxide was added. The solids and ethanol were removed to give *cis*-3,5-dimethylpyrazolidine, b.p. 69° (40 mm.);  $n_D^{25}$  1.4510; 27% yield.

(1) R. J. Crawford, R. J. Dummel, and A. Mishra, *J. Am. Chem. Soc.*, **87**, 3023 (1965).

(2) J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, **28**, 1545 (1963).

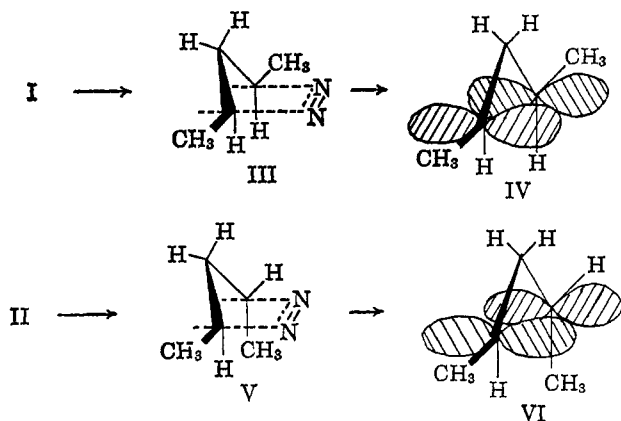
via a transition state resembling III to an intermediate having the geometry IV; II similarly through V to produce an isomeric diradical VI.<sup>5</sup> That I goes pre-

(3) C. G. Overberger, N. Weinshenker, and J. P. Anselme, *J. Am. Chem. Soc.*, **86**, 5364 (1964), have observed similar spectra for *cis*- and *trans*-3,5-bis(*p*-methoxyphenyl)-1-pyrazoline. In I the high-field proton ( $\tau$  9.50) arises from the shielding of the azo link, indicating that the pyrazoline ring is puckered. See J. J. Uebel and J. C. Martin, *ibid.*, **86**, 4618 (1964), for a similar case of shielding by the azo group.

(4) W. von E. Doering and W. Kirmse, *Tetrahedron*, **11**, 272 (1960).

(5) Whether the intermediates IV and VI are diradicals or whether

dominantly to *trans*-1,2-dimethylcyclopropane requires the diradical intermediate to undergo conrotation.<sup>6</sup> Similarly conrotation of VI results in II being transformed into *cis*-1,2-dimethylcyclopropane.<sup>7</sup>



The olefins may be explained by migration of either of the methylene hydrogens in IV to the radical centers giving only *trans*-2-pentene. When either of the methylene hydrogens in VI migrates to C-3 then *trans*-2-pentene is produced, but migration of a hydrogen atom to C-5 results in the formation of *cis*-2-pentene.<sup>8</sup>

That the transition state resembles III and IV is supported by the kinetic data in Table II. The 4,4-

Table II. Kinetics of Pyrazoline Decomposition

1-Pyrazoline	Temp., °C.	10 <sup>4</sup> k, sec. <sup>-1</sup>	Rel. rate
I	197.0	5.42	
II	197.0	8.06	
Unsubstituted	223.0	16.0	1.00
4-Methyl-	223.0	15.5	0.97
4,4-Dimethyl-	223.0	0.126 <sup>a</sup>	0.0079

<sup>a</sup> Extrapolated from rates in the range 250–285°.

dimethyl-1-pyrazoline reacts at less than one-one-hundredth the rate of 1-pyrazoline even though one methyl group introduced into the 4-position has no effect upon the rate. The second methyl group places a methyl on C-4 on the same side as the de-

they are “ $\pi$ -cyclopropanes” wherein they gain some stability by  $\pi$ -bond formation between C-3 and C-5 is not experimentally distinguishable; however, both can serve the purpose of the intermediate. The “ $\pi$ -cyclopropane” would be equivalent to a “hot cyclopropane” with the excess energy localized between C-3 and C-5. If a normal tetrahedral angle is assumed for C-4 then the C-3 to C-5 distance 2.48 Å. results in a Slater overlap integral for  $p_x p_x$  bonds of 0.025, less than one-tenth that of ethylene (see A. Streitwieser, Jr., “Molecular Orbital Theory for Organic Chemists,” John Wiley and Sons Inc., New York, N. Y., 1961, p. 16). Thus the energy gained from overlap approximates that of the repulsion for the two opposed hydrogens. We have thus chosen to refer to the species as a diradical.

(6) R. B. Woodward and R. Hoffman, *J. Am. Chem. Soc.*, **87**, 395 (1965); H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965). Applying the method of Longuet-Higgins and Abrahamson one finds the  $\pi^2$ -configuration of the intermediates (IV and VI) correlate with the  $\sigma^2$ -configuration of the dimethylcyclopropanes no matter whether con- or disrotation is involved.

(7) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc. (London)*, **A257**, 122 (1960), have shown *trans*-1,2-dimethylcyclopropane to be thermodynamically more stable than the *cis* isomer:  $\Delta H = 1.07$  kcal./mole at 380°.

(8) Stereospecific olefin formation in pyrazoline decompositions have recently been observed by D. E. McGreer, *et al.*, *Can. J. Chem.*, **43**, 1407 (1965). They advance a somewhat analogous explanation involving a concerted migration of the hydrogen *trans* to the departing nitrogen.

parting nitrogen in the transition state; thus the reaction rate is decreased by making the desired transition state conformation less accessible.

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## Helium Difluoride

Sir:

We have constructed a many-electron valence bond wave function for HeF<sub>2</sub> and find a repulsive molecular energy curve for all geometries explored. The calculation was carried out using all twenty electrons, the exact, nonrelativistic Hamiltonian within the Born-Oppenheimer approximation, and all terms in the energy expression were consistently evaluated to high precision (eight significant figures). This is the first attempt to make a rigorous and unambiguous theoretical prediction of the properties of noble gas molecules and also represents one of the largest molecules yet treated in such a complete manner. All previous quantum mechanical experience indicates that our wave function is expected to be of high accuracy for this system.

The chemical structures included were<sup>1</sup> F He F, F<sup>-</sup> He<sup>+</sup> F + F He<sup>+</sup> F<sup>-</sup>, F<sup>-</sup> He F<sup>+</sup> + F<sup>+</sup> He F<sup>-</sup>, and F<sup>-</sup> He<sup>2+</sup> F<sup>-</sup>.

In general, each of these structures corresponds to many states differing in orbital occupancy, and the states in turn are composed of sums of 20-row determinantal functions with symmetry-determined coefficients. Symmetric arrangements of atoms on a line lead to 11 states and 33 determinants, asymmetric linear arrays to 18 states and 33 determinants, and off-line equal bond length arrangements to 18 states with 53 determinants. These states represent a complete configuration interaction calculation with a ground-state atomic orbital basis (except for the chemically insignificant excitations of the fluorine 1s electrons). Our molecular wave function is formulated with non-orthogonal atomic orbitals and the energy is expressed in terms of Löwdin's overlap determinants.<sup>2</sup> The atomic orbitals are close to Hartree-Fock solutions and all one- and two-electron, one-, two-, and three-center integrals over these orbitals were evaluated consistently *via* a Gaussian-expansion technique<sup>3</sup> to nine significant figures. Molecular potential energy curves were obtained for three geometrical types: linear symmetric, linear asymmetric, and bent configurations with the He atom midway between the fluorine atoms. Representa-

(1) Structures for He<sup>-</sup> are omitted because helium cannot accept an electron.

(2) P. O. Löwdin, *Phys. Rev.*, **97**, 1474, 1490 (1955).

(3) J. L. Whitten, *J. Chem. Phys.*, **39**, 349 (1963); J. L. Whitten and L. C. Allen, *ibid.*, in press.