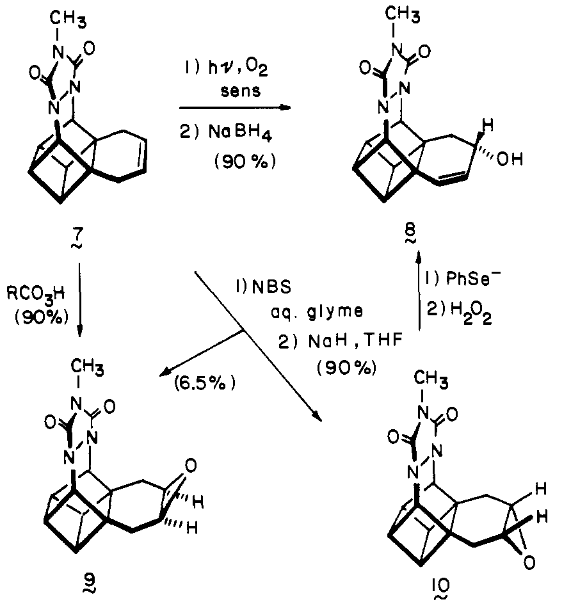
The photooxidations of **1-6** were conducted in a dichloromethane-methanol (9:1) solvent system with rose bengal or methylene blue as sensitizer (comparable stereochemical results). For characterization the hydroperoxides were reduced ($NaBH_4$) without purification to the respective allylic alcohols. Lithium diethylamide promoted ring opening[5] of the epimeric epoxides provided the authentic samples necessary for establishment of stereochemical configuration. With reference to Table I, the data for hydrocarbons **1-5** are seen to parallel precisely the previously established stereoselectivities and reflect the anticipated enhancement of attack from the less congested face of the olefinic plane.[1]



Like photooxygenation of **6** proceeds at a much slower rate than **5** and gives rise only to the product of *opposite* configuration. This most unusual stereochemical reversal involving $^1O_2$ attack from the more sterically encumbered direction appears to be a general reactivity pattern of hydrazides of this type. Thus, the *N*-methyl congener of **6** and the bishomocubane derivative **7** behave comparably!

Pertinent to an understanding of these results are the report by Ouannis and Wilson that $^1O_2$ is efficiently quenched by amines[6] and the finding by Ogryzlo and Tang that there exists a good correlation between the quenching efficiency of the amine and its ionization potential.[7] Briefly summarized, an increase in electron availability is conducive to an increase in k_q. Since the pK_a of a nitrogen base parallels in magnitude its IP and hydrazines are characterized by low pK_a's,[8] such molecules can be expected to be efficient quenchers. Indeed, their effectiveness toward photoexcited ketones has recently been established by Cohen.[9] Because the capability of hydrazides to cause electronic relaxation of $^1\Delta_g$ singlet oxygen was less obvious,[10] the ionization potentials of several representative molecules were measured by photoelectron spectroscopy. The observed IP values (8-8.6 eV)[2,11] are remarkably low and therefore such functional groups are thought to be capable of entering into efficient charge-transfer interaction under the conditions of our experiments.

Based upon such considerations, the "anomalous" behavior of **6, 7,** and related olefins is viewed as the result of efficient deactivation by the hydrazide moiety of $^1O_2$ approach from the more open anti direction. Syn attack can operate without incurring such interactions, although the greater level of steric hindrance leads to an obvious decrease in reactivity.[12]

Acknowledgment. Financial support from the National Cancer Institute (CA-12115) and the Chevron Research Company is gratefully acknowledged. The authors also thank Clifford Lau for technical assistance.

References and Notes

(1) (a) K. Gollnick, *Adv. Photochem.*, **6**, 1 (1968); (b) C. S. Foote, *Acc. Chem. Res.*, 1, 104 (1968); (c) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (d) R. W. Denny and A. Nickon, *Org. React.*, **20**, 133 (1973).

(2) L. A. Paquette, D. C. Liotta, C. C. Liao, T. G. Wallis, N. Eickman, J. Clardy, and R. Gleiter, following paper in this issue.

(3) W. D. Kumler, R. Boikess, P. Bruck, and S. Winstein, *J. Am. Chem. Soc.*, **86**, 3126 (1964).

(4) The epoxidation of (+)-3-carene is a case in point: P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4926 (1966).

(5) J. A. Marshall and R. A. Ruden, *J. Org. Chem.*, **37**, 659 (1972); L. A. Paquette, O. Cox, M. Oku, and R. P. Henzel, *J. Am. Chem. Soc.*, **96**, 4892 (1974).

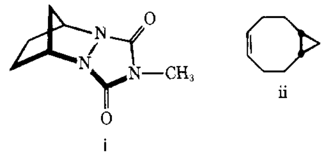
(6) C. Ouannis and T. Wilson, *J. Am. Chem. Soc.*, **90**, 6527 (1968).

(7) E. A. Ogryzlo and C. W. Tang, *J. Am. Chem. Soc.*, **92**, 5034 (1970).

(8) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution", London, 1965; E. Hayon and M. Simic, *J. Am. Chem. Soc.*, **94**, 42 (1972).

(9) S. Ojanpera, A. Parola, and S. G. Cohen, *J. Am. Chem. Soc.*, **96**, 7379 (1974).

(10) In related work, the capability of hydrazides (e.g., i) to appreciably reduce $^1O_2$ reactivity in binary mixed solutions (CH_1Cl_2–CH_3OH, CH_2Cl_2–CH_3CN, CH_2Cl_2) with ii has been demonstrated.



(11) R. Gleiter, private communication.

(12) For example, **5** undergoes complete allylic hydroperoxidation in 2 h while **6** reacts only to 67% completion after 22 h.

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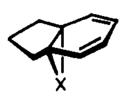
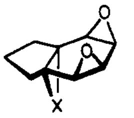
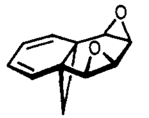
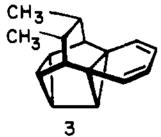
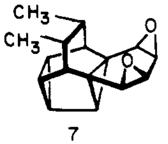
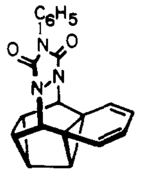
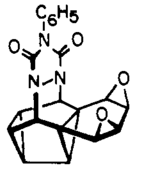
Endoperoxidation of Conformationally Fixed Norcaradienes by Singlet Oxygen. Frontier Molecular Orbital Basis for the Operability of $^1O_2$ Quenching by Hydrazides

Sir:

Just as study of the allylic hydroperoxidation of various 3-norcarenes has revealed the capability of hydrazides to quench $^1\Delta_g$ oxygen as it functions in this reaction,[1] so the endoperoxidation of structurally related norcaradienes should similarly lend itself to an evaluation of a possible hydrazide directive effect on such (4 + 2) cycloadditions. Significantly, the stereochemical outcome of the two oxygenation modes should *not* be identical if the conditions of HMO perturbation theory are rigorously adhered to.

The stereospecificity of norcaradiene endoperoxidation has been experimentally assessed in five different systems (Table I), two of the illustrated examples (**1b**, **2**) having been independently studied by others.[2,3] To facilitate product identification, the first-formed endoperoxides were thermally rearranged to their trishomobenzenoid diepoxide isomers without loss of configuration.[4] Because ^1H NMR data revealed the cyclopropyl protons in the diepoxides to be only marginally shielded, the oxygen atoms are assumed to be anti to the three-membered ring. This important stereochemical point was established conclusively by x-ray crystal structure analysis of **8** (Figure 1), the crystals of which form in the orthobombic system with $a = 13.404$, $b = 15.147$ (3), and $c = 16.020$ (4) Å. Systematic extinctions in $0kl$ (absent if $k = Zn + l$), $h0l$ (absent if $l = Zn + l$), and $hk0$ (absent if $h = Zn + l$) sug-

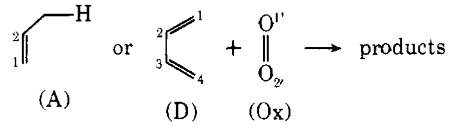
Table I. Results of Norcaradiene Endoperoxidation[a]

Diene	Diepoxide[b]	^{1}H NMR (δ, $CDCl_3$)
 1a, X = CH_2 b, X = O	 5a, X = CH_2 b, X = O	(5a) 3.33 (s, 4), 2.23–1.60 (m, 6), 0.78 (d, J = 5 Hz, 1), 0.47 (d, J = 5 Hz, 1) (5b)[c] 3.4 (s, 4), 2.2–1.4 (m, 6)
 2	 6	6.12 (m, 4), 3.55 (m, 2), 3.43 (m, 2), 1.63 (d, 1), −0.04 (d, 1)[d]
 3	 7	3.42 (d, J = 3.5 Hz, 2), 3.37 (d, J = 3.5 Hz, 2), 2.57–1.47 (m, 6), 1.31–0.80 (m, with d centered at 0.93 Hz, J = 7 Hz, 8)
 4	 8	(C_5D_5N), 7.97 (dd, J = 8 and 1.5 Hz, 2), 7.46–7.21 (m, 3), 5.23 (t, J = 2.5 Hz, 2), 3.35 (d, J = 2.8 Hz, 2), 3.14 (dd, J = 2.8 and 1.1 Hz, 2), 2.17–1.94 (m, 4)

[a] Various solvents (CH_3OH, CH_2Cl_2, CH_3COCH_3) have been employed in the $^1O_2$ reaction with either rose bengal or methylene blue as sensitizer. The endoperoxides were rearranged in chloroform or 1,2-dichloroethane at the respective reflux temperatures. [b] In all cases, the illustrated diepoxide was the only product detected. [c] See ref 2. [d] See ref 3.

gested space group P_{bca} and a measured and calculated (Z = 8) density indicated one unit of composition $C_{20}H_{15}N_3O_4$ formed in the asymmetric unit. Using graphite monochromated Cu Kα radiation, 1747 reflections were judged observed after suitable correction and full-matrix least-squares refinement converged to the unweighted residual 0.043.[5,6] See paragraph at end of paper regarding additional supplementary material.

Despite its shortcomings,[7] frontier molecular orbital theory[8] is recognized to provide a most useful framework by which the energies (E) and coefficients (C) of the highest occupied (HO) and lowest unoccupied (LU) orbitals of two reacting molecules can be related directly to stabilization energy (ΔE) as well as relative rate for several reaction types.[9] Equations 1 and 2 treat the general case for $^1O_2$ as it enters into ene reaction or (4 + 2) cycloaddition with an appropriate alkene (A)[10] or diene (D). For simplification purposes,[10] we assume that the eigenvectors of the coefficients in the numerators remain reasonably constant when a series of closely related alkenes or dienes is studied. To a first approximation then, the transition state energies become a function chiefly of the orbital energy differences. Since inspection of the ionization potential (−11.09 eV)[11] and electron affinity (−0.43 eV) data[12] reported for oxygen as well as for olefins and dienes which are reactive toward $^1O_2$[13] indicates further that the only significant frontier orbital interaction is that between the olefin or diene HOMO and the singlet oxygen LUMO, ultimate simplification to eq 3 and 4 results (c is a constant).



$$\Delta E = \frac{[(C_{HO1'}C_{LU1} + C_{HO2'}C_{LU2})\beta]^2}{(E_{OxHO} - E_{ALU})} + \frac{[(C_{HO1}C_{LU1'} + C_{HO2}C_{LU2'})\beta]^2}{(E_{AHO} - E_{OxLU})} \tag{1}$$

$$\Delta E = \frac{[(C_{HO1'}C_{LU1} + C_{HO2'} - C_{LU4})\beta]^2}{(E_{OxHO} - E_{DLU})} + \frac{[(C_{HO1'}C_{LU1} + C_{HO4} - C_{LU2'})\beta]^2}{(E_{DHO} - E_{OxLU})} \tag{2}$$

$$\Delta E = (c\beta)^2/(E_{AHO} - E_{OxLU}) \tag{3}$$

$$\Delta E = (c\beta)^2/(E_{DHO} - E_{OxLU}) \tag{4}$$

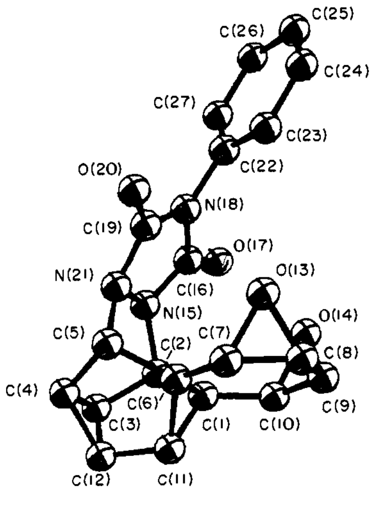


Figure 1. Computer generated drawing of the x-ray model of 8. Although all bond distances and angles are normal, the unusual canting of the urazole ring toward the epoxide oxygens should be noted.

The electronic constitutions of a number of key compounds as revealed by ionization potential data obtained from photoelectron spectroscopic measurements are illustrated in Figure

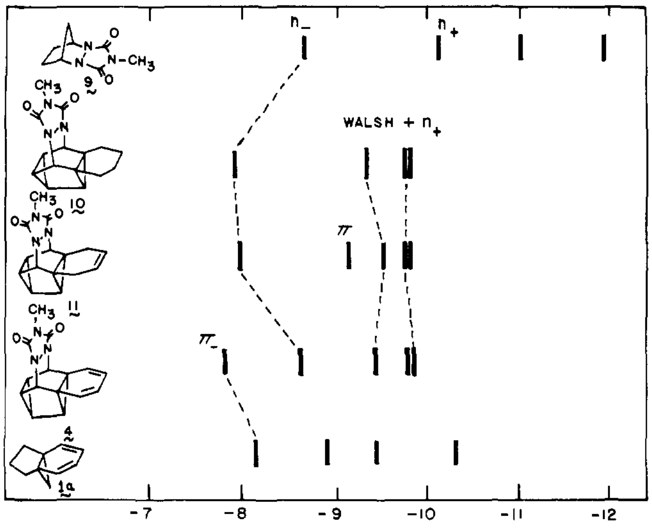
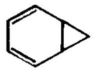


Figure 2. Photoelectron spectroscopy results.

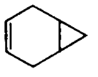
2. Concerning urazoles **9–11**, the HOMO's are readily assignable as the respective a_2 (n_-) bands (−8.6, −7,9, and −7.95 eV). For **4**, the $\pi_- + e_A$ (antisymmetric cyclopropane Walsh orbital) interaction is considered to be of primary importance. However, secondary interaction between the n_- and the in-phase and out-of-phase norcaradiene orbitals ($\pi_- - e_A$, $\pi_- + e_A$) causes a further destabilization of $\pi_- - e_A$ with concomitant enhanced stabilization of $\pi_- + e_A$. Since the companion energy change in n_- happens to be negligible relative to **9**,[14] the important net result is a dramatic destabilization of π_- such that it becomes the HOMO in **4**.

The significance of this phenomenon is that conventional approach of $^1O_2$ to the sterically more accessible anti surface of **4**



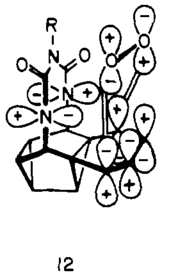
I

results in preferred $HOMO_I$-$LUMO_{O_2}$ interaction (−7.8 − (−0.4) = −7.4 eV) and endoperoxide formation (see **12**). In this instance, the $HOMO_{NN} - LUMO_{O_2}$ gap (−8.2 eV) is too large by comparison to exert any effect. But with norcarene **11**, $^1O_2$ attack from the sterically favored anti direction leads to efficient quenching because interaction with the hydrazide moiety ($HOMO_{NN} - LUMO_{O_2}$ = −7.5 eV, cf. **13**)[15] is vastly more energetically rewarding than the alternative $HOMO_{II}$

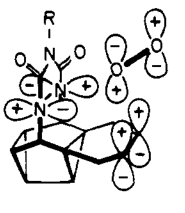


II

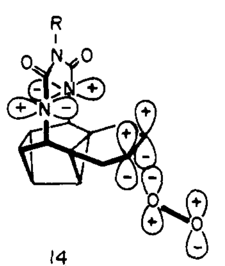
− $LUMO_{O_2}$ option (−8,7 eV). No such quenching can occur upon syn attack as in **14**, but steric hindrance can be expected to cause kinetic retardation as is seen.[1]



12



13



14

Thus, antisymmetric charge-transfer interaction between $HOMO_{NN}$ and $LUMO_{O_2}$ is seen to comprise an entirely plausible quenching mechanism. Because singlet and triplet charge transfer complexes are energetically similar, relatively low level spin-orbit coupling is probably sufficient to mix the interacting states.[17] The unusually low activation energies for $^1O_2$ reactions (0.1-7.5 kcal/mol)[4,18] also undoubtedly contribute to its sensitivity to electronic perturbation.[13,17b,19]

In summary, frontier MO theory has now been shown to be a valuable tool in assessing the regio-[13] and stereospecificity of singlet oxygen behavior during ene and (4 + 2) cycloaddition reactions. Further applications of this discovery to other reaction modes and to alternate substrate modifications are under active investigation.

Acknowledgment. Financial support from the National Cancer Institute (CA-12115) is gratefully acknowledged.

Supplementary Material Available: The crystallographic data for **8** (fractional coordinates (Table I), bond distances (Table II), bond angles (Table III), and observed and calculated structure factors (Table IV)) (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) L. A. Paquette, C. C. Liao, D. C. Liotta, and W. E. Fristad, preceding communication.
(2) C. H. Foster and G. A. Berchtold, *J. Org. Chem.*, **40,** 3743 (1975).
(3) E. Vogel, A. Alscher, and K. Wilms, *Angew. Chem., Int. Ed. Engl.*, **13,** 398 (1974). See also D. Ginsburg, "Propellanes", Verlag Chemie, Weinheim, West Germany, 1975, p 117.
(4) R. W. Denny and A. Nickon, *Org. React.*, **20,** 133 (1973).
(5) Solution using a multiple solution weighted tangent formula approach was routine: P. Main, M. Woolfson, and G. Germain, MULTAN, Department of Physics, University of York, York, England, 1971.
(6) The following library of crystallographic programs was used: C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, "The Fast Fourier Algorithm and the Programs ALFF, ALFFDP, ALFFT, and FRIEDEL", USAEC Report IS-2625, Iowa State University-Institute for Atomic Research, Ames, Iowa, 1971; W. R. Busing, K. O. Martin, and H. A. Levy, "A Fortran Crystallographic Least Squares Program", USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965; C. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program", U.S. Atomic Energy Commission Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(7) G. Klopman, *J. Am. Chem. Soc.*, **90,** 223 (1968); L. Salem, *ibid.*, **90,** 543, 553 (1968); A. Devaquet and L. Salem, *ibid.*, **91,** 3793 (1969); R. Sustmann and G. Binsch, *Mol. Phys.*, **20,** 9 (1971); G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, **8,** 165 (1967).
(8) E. Heilbronner and H. Bock, "Das HOMO-Modell und Seine Anwendung", Verlag Chemie, GmbH, Weinheim/Bergstr., 1970; M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969; K. Fukui, *Fortschr. Chem. Forsch.*, **15,** 1 (1970); "Chemical Reactivity and Reaction Paths", J. Klopman, Ed., Wiley-Interscience, New York, N.Y., 1974; K. Fukui, *Acc. Chem. Res.*, **4,** 57 (1971).
(9) As examples, we cite: (a) (4 + 2) cycloadditions R. Sustmann and R. Schubert, *Angew. Chem., Int. Ed. Engl.*, 11, 840 (1972); (b) 1,3-dipolar additions, R. Sustmann and H. Trill, *ibid.,* 11, 838 (1972); (c) polar additions: N. A. Porter, I. G. Westerman, T. G. Wallis, and C. K. Bradsher, *J. Am. Chem. Soc.*, **96,** 5104 (1974); (d) (2 + 2) cycloadditions, K. N. Houk, *Acc. Chem. Res.*, **8,** 361 (1975).
(10) Such assumptions have previously been utilized extensively.[9]
(11) N. Jonathan, D. Smith, and K. Ross, *J. Chem. Phys.*, **53,** 3758 (1970); R. J. McNeal and G. R. Cook, *ibid.*, **45,** 3469 (1966).
(12) As determined for triplet oxygen: J. L. Pack and A. V. Phelps, *J. Chem. Phys.*, **44,** 1870 (1966).
(13) L. A. Paquette, D. C. Liotta, and A. D. Baker, *Tetrahedron Lett.*, 2681 (1976). Professor C. W. Jefford (Geneva) has privately informed us (March 23, 1976) that he has uncovered a similar relationship in a series of norbornene derivatives.
(14) A direct result of the fact that the n_- level (−8.6 eV) which is positioned almost exactly midway between π_- (−8.25 eV) and e_A (−9.08 eV) experiences essentially equal but opposite influences which cancel.
(15) Since both $1\pi_g$ orbitals of $^1O_2$ are antibonding and antisymmetric as well as degenerate [see W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973, p 88, for an orbital representation of triplet oxygen], alternative formulations of **12–14** showing the oxygen orbitals rotated by 90° about the O–O axis can be drawn as well. We emphasize that the present rontier MO analysis is extra-mechanistic,[1] meaning that although "peroxirane-like" transition states are pictured in **13** and **14** because of their current popularity with theoretical chemists,[16] this mechanism is not demanded by our analysis.
(16) S. Inagaki, S. Yamabe, H. Fujimoto, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **45,** 3510 (1972); M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **97,** 3978 (1975); S. Inagaki and K. Fukui, *ibid.*, **97,** 7480 (1975).
(17) (a) M. A. ElSayed, *J. Chem. Phys.,* **46,** 572 (1967); (b) E. A. Ogryzlo and C. W. Tang, *J. Am. Chem. Soc.*, **92,** 5034 (1970).

(18) R. D. Ashford and E. A. Ogryzlo, *J. Am. Chem. Soc.*, **97**, 3604 (1975).
(19) C. Ouannès and T. Wilson, *J. Am. Chem. Soc.*, **90**, 6527 (1968).
(20) Camille and Henry Dreyfus Teacher-Scholar Grant Awardee 1972–1977 and Fellow of the Alfred P. Sloan Foundation 1973–1975.

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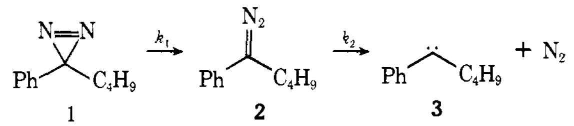
Received April 26, 1976

Mechanism of Thermal Decomposition of Diazirine. Evidence for Diazomethane Intermediate

Sir:

The intermediacy of diazomethane in the decomposition of diazirine has been the subject of discussion for many years.[1-3] While there is sufficient evidence for the diazomethane intermediate in the photolysis of diazirine,[4] its presence in the thermal decomposition has only been implicated, and no diazomethane intermediate has ever been isolated from a diazirine pyrolysis experiment.[5-7] In one report,[8] the attempted synthesis of 3,3-diphenyldiazirine resulted in the formation of diphenyldiazomethane; however, the precursory existence of diazirine was never verified. Only in the case of 3-methyl-3-vinyldiazirine has the linear diazo isomer been observed[7] as its subsequent reaction product, 3-methylpyrazole. We wish to report here evidence for the formation of 1-phenyl-1-diazopentane (**2**) in the thermolysis of 3-*n*-butyl-3-phenyldiazirine (**1**). This represents, to the best of our knowledge, the first account of the isolation of a diazomethane from the thermolysis of a simple diazirine and serves to support the mechanism for diazirine decomposition shown in Scheme I.

Scheme I



Diazirine **1** was synthesized in 40% overall yield from valerophenone by the method of Schmitz and Ohme.[9,10] Thermolysis of dilute Me_2SO solutions (0.1 M) of **1** at 100 °C for 3 h resulted in a quantitative evolution of nitrogen (measured by gas burette) and the formation of *cis*- and *trans*-1-phenyl-1-pentenes (ratio cis:trans = 1:5, determined by GLC) plus a small amount (<5%) of valerophenone, all (presumably) via carbene **3**. Surprisingly, no azine was detected.[11] When the reaction was followed by uv or ir spectroscopy, an intermediate species was observed to form rapidly and subsequently diminish; uv_{max} at 500 nm (low ϵ) and ir_{max} at 4.90 μ are consistent with this intermediate being assigned and the diazo structure **2**. Interruption of the reaction after 1 h followed by extraction with petroleum ether (30-60 °C) permitted the isolation of **2** along with unreacted **1** and small quantities of the 1-phenyl-1-pentenes. Compound **2** appears to be very stable, as the red petroleum ether solution remained unchanged at room temperature for several days. Addition of acetic acid to the red solution resulted in immediate discoloration and subsequent isolation of 1-phenyl 1-pentylacetate.[12]

Table I. First-Order Rate Constants at 100.2 °C

Solvent	Uv method 10^4k_1 (s^{-1})	N_2 evolution 10^4k_2 (s^{-1})
Me_2SO	6.75 ± 0.02	2.23 ± 0.16
HOAc	5.24 ± 0.07	5.78 ± 0.19

The rate of decomposition of **1** at 100.2 °C was determined by measuring the disappearance of it's uv_{max} at 371 nm (k_1) and by measuring the evolved nitrogen during the reaction (k_2).[13] The first-order rate constants are presented in Table I. That the two measurements in Me_2SO solvent differ by a factor of three suggests that in fact two different rates are being measured; k_1 can therefore be taken as the rate of isomerization of **1** to **2**, while k_2 may be regarded as the rate of decomposition of **2**, giving nitrogen and **3**. As such, k_1 is in good agreement with reported rate constants for decomposition of other diazirines,[6] while k_2 agrees with the reported rate constant for thermal decomposition of diphenyldiazomethane.[14]

The assignment of k_1 and k_2 above finds further support in their measurement in acetic acid (Table I). It is well established that diazirine decomposition is unaffected by acid[1] while the decomposition of diazomethanes is acid catalyzed.[15] Thus in this case, the isomerization of **1** to **2** would be the rate determining step in the overall reaction and k_2 would be expected to equal k_1, which is the experimental observation. Workup of the acetic acid reaction mixture resulted in the isolation of 1-phenyl 1-pentylacetate in 75% yield, and a mixture of *cis*- and *trans*-1-phenyl-1-pentenes in 20% yield.

The evidence reported here clearly establishes that the primary mode of diazirine decomposition is via its linear diazo isomer, as shown in Scheme I, although we cannot at present completely rule out the possibility that decomposition also occurs via a minor pathway directly to carbene. Kinetic experiments on this system are in progress to further clarify these points.

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References and Notes

(1) E. Schmitz, *Angew. Chem., Int. Ed. Engl.*, **3,** 333 (1964).
(2) W. Kirmse, "Carbene Chemistry", Academic Press, New York, N.Y., 1971.
(3) C. H. Bramford and C. F. H. Tipper, "Comprehensive Chemical Kinetics", Vol. 5, Elseview Publishing Company, New York, N.Y., 1972.
(4) R. A. Smith and J. R. Knowles, *J. Chem. Soc., Perkin Trans. 2*, 686 (1975); H. M. Frey, *Adv. Photochem.*, **4,** 225 (1966).
(5) E. Schmitz, C. Horig, and C. Grundemann, *Chem. Ber.*, **100,** 2093 (1967); E. W. Neuvar and R. A. Mitsch, *J. Phys. Chem.*, **71**, 1229 (1967).
(6) M. T. H. Liu and K. Toriyama, *Can. J. Chem.*, **50**, 3009 (1972); *J. Phys. Chem.*, **76,** 797 (1972); *Can. J. Chem.*, **51,** 2392 (1973); M. T. H. Liu and D. H. T. Chien, *J. Chem. Soc., Perkin Trans. 2*, 937 (1974).
(7) E. Schmitz, "23rd International Congress of Pure and Allied Chemistry", Vol. II, Butterworths, London, 1971, p 283.
(8) C. G. Overberger and J-P. Anselme, *Tetrahedron Lett.*, 1405 (1963).
(9) E. Schmitz and R. Ohme, *Chem. Ber.*, **95,** 795 (1962).
(10) Uv_{max} (hexane) 371 (ϵ 234), 382 nm (ϵ 214); ir (CCl_4) 6.35 (N=N) μ; NMR (CCl_4) τ 2.8 (m, 3), 3.13 (m, 2), 8.07 (br t, 2), 8.7 (m, 4), 9.1 (br t, 3); *m/e* 146 ($M^+ - 28$).
(11) C. G. Overberger and J-P. Anselme, *J. Org. Chem.*, **29,** 1188 (1964).
(12) Spectral data: ir (CCl_4) 5.74)c=O) μ; NMR (CCl_4), τ 2.77 (s, 5 aromatic), 4.35 (t, 1, J = 6.5 Hz, methine), 8.04 (s, 3, methyl), 8.2 (m, 2), 8.7 (m, 4), 9.13 (t, 3, J = 6 Hz, methyl); *m/e* parent 206.
(13) The determination of k_2 in Me_2SO by N_2 evolution method requires elaboration. The first-order plot from N_2 measurements does not give a straight line; in fact, there is a slight curvature (convex) during the first 20–30 min of the reaction. This curvature is due to the buildup of the diazo compound. After such time, N_2 evolution begins to approximate first-order behavior and it is in this portion of the graph that k_2 was taken. In order to confirm the value of k_2, we have synthesized 1-phenyl-1-diazopentane from a separate experiment, and its N_2 evolution in Me_2SO was measured. The first-order rate constant determined in this manner was within 3% of the value reported in Table I.