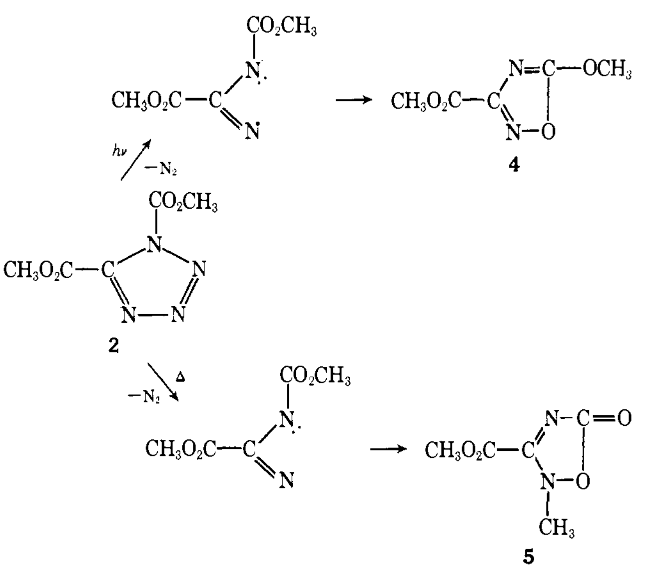
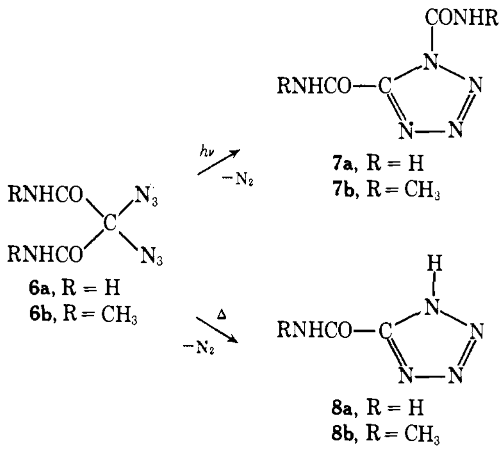
Scheme II



ferring hydrogen to nitrogen in the case of both **6a** and **6b** to yield **8a** and **8b**, respectively.

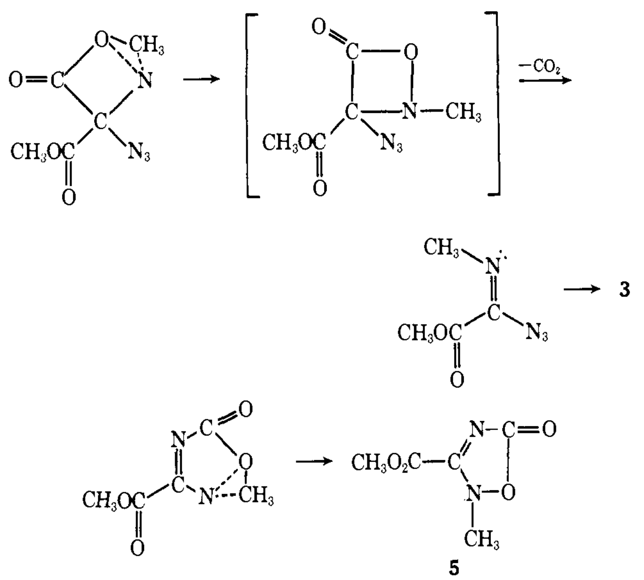


This is the first example of a unique and exclusive difference in the two modes of decomposition of azides. The pattern which emerges is that the photochemical reaction of either the diazides or tetrazoles[7,8] involves migration, whereas the thermal decomposition shows a preference for insertion.

Our view of the photochemical decomposition of alkyl azides is that migration of the α substituent is concerted with loss of nitrogen. The discrete nitrene has no real existence and the group which migrates is determined by ground-state conformational structures. Concisely, rotational equilibration is slower than the Franck–Condon controlled photoexcitation. The thermal reaction is characterized by the adoption of a transition state in which insertion of the nitrenoid nitrogen into the carbon–oxygen bond may occur.

The two thermal reactions may be represented by the following intermediates or transition states for the thermal decomposition of **1** and **2**, respectively (Scheme III).

Scheme III



The thermal loss of nitrogen from the tetrazole proceeds through a $4n + 2\pi$ electron transition state which is isoconjugate with the cyclopentadienate anion. This process should be concerted and lead directly to a singlet nitrene. The photoreaction proceeds *via* an excited state which is antiaromatic. The five atomic orbitals of the excited state possess a phase discontinuity and therefore it is isoconjugate with the cyclobutadiene system. This process is therefore nonconcerted and may yield the triplet state of the nitrene by a stepwise path.

Acknowledgment. We thank the National Science Foundation for support of this work under Grant No. NSF GP-18113.

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Received October 24, 1970

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Nuclear Magnetic Resonance Studies of Long-Range Fluorine Spin Couplings

Sir:

The relative importance of "through-space" and "through-bond" interactions in determining the overall magnitude of long-range $^1H-^{19}F$ spin–spin coupling has not been convincingly established.[1-3] Detailed studies of the five-bond F–F coupling in a series of substituted 4,5-difluorophenanthrenes[4] led to the firm conclusion that through-space interaction of the fluorine nuclei predominates in long-range F–F coupling.[5,6] A similar approach to the study of long-range H–F coupling did not appear attractive because of the expected much smaller magnitude of the long-range H–F coupling

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(5) (a) R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Tetrahedron*, **26**, 71 (1970); (b) R. D. Chambers, L. H. Sutcliffe, and G. J. T. Tiddy, *Trans. Faraday Soc.*, **66**, 1025 (1970).

(6) As expected for through-space interaction, the signs of these long-range F–F coupling constants are found to be positive.[5b]

constants.[7] Instead we have sought to evaluate the importance of through-space contributions to H–F coupling by determining whether long-range H–F and F–F coupling constants show comparable stereochemical dependence in related compounds. We now wish to report that long-range F–F coupling exhibits a dramatic dependence on geometry and that long-range methyl hydrogen to fluorine coupling behaves proportionately.

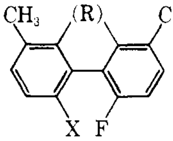
Osmium tetroxide oxidation[8a] of 1,8-dimethyl-4,5-difluorophenanthrene (**1**-F) gave in 90% yield *cis*-1,8-dimethyl-4,5-difluoro-9,10-dihydro-9,10-phenanthrenediol (**2**-F). The 94.1-MHz $^{19}F-\{^1H\}$, proton decoupled spectrum of **2**-F in tetrahydrofuran solvent exhibited a single ^{19}F resonance at 51.7 ppm (downfield from hexafluorobenzene). Upon cooling the sample, this resonance progressively broadened and eventually resolved into a typical A–B pattern with $^5J_{F-F} = 98$ Hz; $\delta_A - \delta_B = 1.77$ ppm. This behavior is clearly indicative of the slowing of the interconversion of the nonplanar enantiomeric forms of **2**-F. As expected for a through-space coupling mechanism, increasing the fluorine–fluorine distance as occurs in the conversion of **1**-F to **2**-F (*vide infra*) produces a dramatic decrease in the F–F coupling: $^5J_{F-F}{}^{1-F} - {}^5J_{F-F}{}^{2-F} = 72$ Hz!

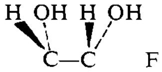
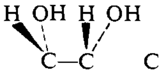
1,4,8-Trimethyl-5-fluorophenanthrene (**1**-CH_3) was synthesized in 30% overall yield starting from 2-iodo-4-fluorotoluene and 2,5-dimethylbenzyl chloride by following the procedure published previously.[4] Osmium tetroxide oxidation[8a] of **1**-CH_3 gave *cis*-1,4,8-trimethyl-5-fluoro-9,10-dihydro-9,10-phenanthrenediol (**2**-CH_3). Oxidation of **1**-CH_3 with chromium trioxide in acetic acid[8b] gave, in 70% yield, 1,4,8-trimethyl-5-fluoro-9,10-phenanthrenequinone (**3**-CH_3); as a by-product of this reaction, the corresponding diacid anhydride (**4**-CH_3) was obtained in 20% yield.

Chemical shifts and coupling constants determined for **1**-F, **2**-F, **1**-CH_3, **2**-CH_3, **3**-CH_3, and **4**-CH_3 are summarized in Table I. Fluorine decoupling served to verify the assignments of observed splittings as resulting from H–F spin–spin coupling. For **1**-CH_3, ^{19}F double irradiation ($^1H-\{^{19}F\}$) collapsed the C_8-methyl doublet ($J = 1.1$ Hz)[9] and the C_4-methyl doublet ($J = 11.9$ Hz) to singlets and produced typical A–B patterns for both the 9,10 and 6,7 hydrogen pairs. For both methyl group couplings, the hydrogen and fluorine nuclei are separated by six bonds. The 4-CH_3, 5-F coupling of 11.9 Hz appears to be the largest $^6J_{H-F}$ reported to date.[10] Saturation of the 9,10 double bond, as in **2**-CH_3, results in a marked decrease in this coupling constant: $J_{4-CH_3,5-F}{}^{2-CH_3} = 7.7$ Hz.

Dreiding models of **1**-F, **2**-F, **1**-CH_3, and **2**-CH_3 indicate that severe steric interactions between the groups at the 4 and 5 positions result in large deviations from planarity.[11] As a result of differences in torsional strains, deviations from planarity should be smaller for the parent phenanthrenes, **1**-F and **1**-CH_3, than in the 9,10-dihydro derivatives, **2**-F and **2**-CH_3. The consequence should therefore be a greater proximity of atoms at positions 4 and 5. This effect is reflected in the chemical shifts of the methyl groups at position 4. As the molecule deviates from planarity, the methyl group moves into the positive shielding cone of the other aromatic ring and an upfield shift of the methyl group results ($\delta_{4-CH_3}{}^{2-CH_3} - \delta_{4-CH_3}{}^{1-CH_3} = 0.37$ ppm).

Table I. Coupling Constants and Chemical Shifts for Derivatives of 4,5-Difluoro- and 4-Fluoro-5-methylphenanthrenes[a,b]



Compd	R	X	$J_{4-F,5-X}$	δ_{4-F}	δ_{5-X}	δ_{1-CH_3}	δ_{8-CH_3}
1-F	$-CH{=}CH-$	F	170[e]	59.0	59.0	2.58	2.58
2-F		F	98	51.7	51.7	2.46	2.46
1-CH_3[d]	$-CH{=}CH-$	CH_3	11.9		2.59	2.54	2.56
2-CH_3		CH_3	7.7[c]		2.22	2.50	2.50
3-CH_3	$O{=}CC{=}O$	CH_3	8.2		2.23	2.55	2.55
4-CH_3	$O{=}COC{=}O$	CH_3	3.7		2.23	2.41	2.43

[a] Determined from ^1H and ^{19}F nmr spectra at 100 and 94.1 MHz, respectively. [b] ^1H chemical shifts are reported in parts per million downfield from internal tetramethylsilane; ^{19}F chemical shifts are reported in parts per million downfield from internal hexafluorobenzene. All coupling constants are reported in hertz. [c] Determined from the ^1H nmr spectrum at 60 MHz. [d] The following additional nmr parameters were determined: $\delta_{H_6} = \delta_{H_7} = 7.22$, $\delta_{H_7} = 7.02$, $\delta_{H_3} = 7.19$, $\delta_{H_{10}} = 7.53$, $\delta_{H_9} = 7.65$; $J_{2,3} = 7.9$, $J_{9,10} = 9.1$, $J_{1,4} = 1.1$, $J_{2,4} = 5.4$, $J_{3,4} = 12.4$, $J_{4,10} = 2.1$ Hz. [e] Reference 4.

The changes in proximity of the groups at the 4 and 5 positions are also reflected in changes in the fluorine coupling constants. The decrease in J_{F-F} can be taken as a standard fractional decrease in through-space coupling as a consequence of this structural variation: $J_{F-F}{}^{2-F}/J_{F-F}{}^{1-F} = 0.57$. The observation that H–F coupling decreases by a comparative amount, $J_{CH_3,F}{}^{2-CH_3}/J_{CH_3,F}{}^{1-CH_3} = 0.64$, implies that through-space interaction contributes substantially to the 4-methyl, 5-fluoro coupling constant. Such coupling may result from interactions centered on the fluorine and methyl–carbon nuclei rather than directly between the fluorine and hydrogen nuclei.[12,15] Further studies of fluorine coupling in these and related systems are currently in progress and will be reported shortly.

Acknowledgment. We wish to thank the Research Corporation for financial assistance. Grants from the

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(11) If the phenanthrene ring were planar, the distance of closest approach between hydrogen and fluorine in **1**-CH_3 would be 0.4 Å and between fluorine and fluorine in **1**-F would be 1.5 Å. The corresponding distances in the 9,10-dihydro compounds would be 0.6 Å in **2**-CH_3 and 1.7 Å in **2**-F, respectively.

(12) This would account for the absence of 5-H,4-F coupling in 4-fluorophenanthrenes[13] and might contribute to the unusual dihedral angle dependence of – H,F coupling in *o*-alkylfluorobenzenes.[14]

(13) K. L. Servis and K.-N. Fang, unpublished results.

(14) The α-H,F coupling in *o*-alkylfluorobenzenes appears strongest when α-H is not proximate to fluorine: P. C. Myhre, personal communication.

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National Science Foundation aided in the purchase of nmr spectrometers used in this work.

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Photodecomposition of Alkyl Azides. Absence of Freedom of Choice and Nonnitrene Mechanism

Sir:

Photolysis of alkyl azides has usually been thought to involve the formation of nitrene intermediates which then rearrange to imines.[1] This was supported by the observation[2] that in tertiary azides no preference was observed for methyl *vs.* phenyl *vs.* substituted phenyl migration in unsensitized photolyses, suggesting the formation of a highly reactive nitrene intermediate without any alkyl or aryl participation. In earlier work, we had observed a definite, though small, preference for methyl over 2-biphenylyl migration in the photolysis of 1-biphenyl-2-yl-1-methylethyl azide (**6**),[3] and now present evidence for nonstatistical migration of alkyl and aryl groups in the photolysis of alkyl azides, which proves that a discrete nitrene intermediate is *not* formed in these reactions and that migration starts before the N–N bond is completely cleaved. In addition, we show that the reactive intermediate is not free to choose which of the groups it would, for electronic reasons, prefer to attack. Very recently, Moriarity and Reardon[4] concluded also that rearrangement concerted with elimination of nitrogen is occurring. Since our results and our model for the photochemical process differ from theirs we describe these here.

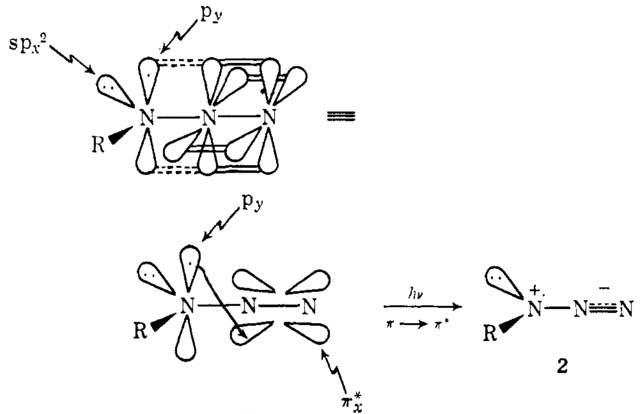
Table I. Migratory Aptitudes[a] in the Photolysis of *tert*-Alkyl Azides

Ph-Me[b]	Ar-Me[c]	Ar-Ph[d]	$PhCH_2CH_2$-Me[e]
0.75	0.69	0.44	0.89

[a] Corrected for statistical preference. Photolyses carried out to low conversions (*ca.* 5%) in cyclohexane solution at room temperature using a medium-pressure lamp and a Vycor vessel. Products analyzed directly by glc at various intervals of time. [b] From 2-phenyl-2-propyl azide. Previously reported[2a] value of 0.96. [c] Ar = 2-biphenyl, from 1-biphenyl-2-yl-1-methylethyl azide (**6**). Previously reported[3] value 0.43. [d] Ar = 2-biphenylyl, from 2-biphenylyldiphenylmethyl azide. [e] From 2-azido-2-methyl-4-phenylbutane.

Table I records the migratory aptitudes obtained from the photolysis of several tertiary alkyl azides. These are not statistical, the smaller group migrating preferentially in each case. It is also clear that the electron-deficient reactive intermediate is not free to attack the more nucleophilic group. These results are best explained in terms of the preferred ground-state conformations of the azides[4,5] and the geometry of the orbitals in the photoexcited state of the azido group.[5]

It has been reported[6] that the electronic transition (287 nm) normally involved in the photoexcitation of alkyl azides is $\pi_y \rightarrow \pi_x^*$ (**1** → **2**). This would leave the p_y orbital on the α-nitrogen atom electron deficient.[7] If this is so, then a concerted migration–elimination would not involve backside (trans) attack[4]



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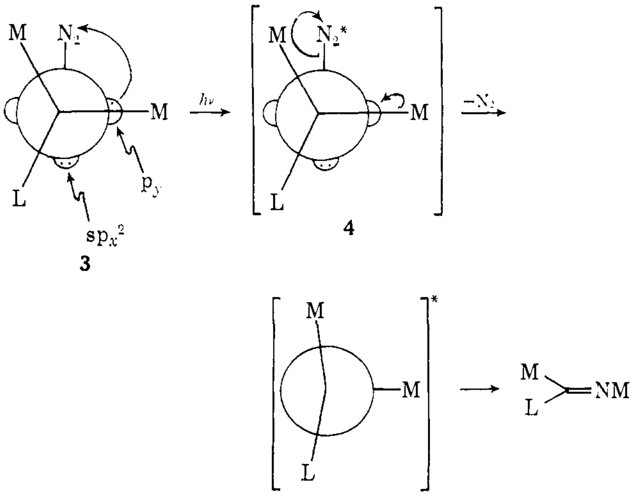
(which would require migration to a filled sp_x^2 orbital) but rather the migrating and departing groups would be orthogonal to each other, **4**, so that the bonding orbital of the migrating group would overlap with the electron-deficient p_y orbital.[9] If one further assumes the Franck–Condon principle to hold in these photolyses, then the preferred ground-state conformation of the alkyl azide would determine which group would be suitably oriented to migrate.



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