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

(16) Alfred P. Sloan Research Fellow, 1969–1971.

(17) National Science Foundation Trainee, 1968–1970.

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Received November 30, 1970

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.

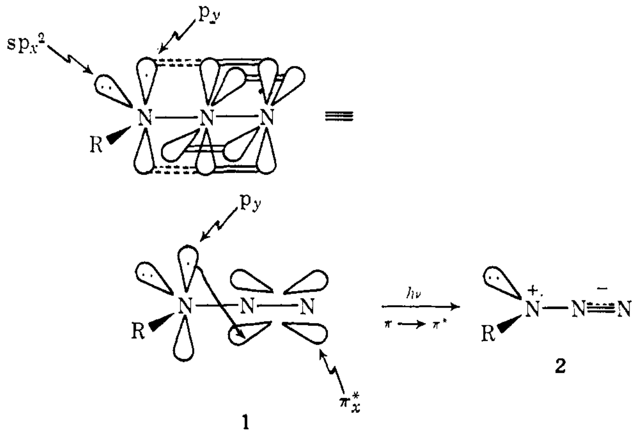
Table I. Migratory Aptitudes[a] in the Photolysis of *tert*-Alkyl Azides

Ph-Me[b]	Ar-Me[c]	Ar-Ph[d]	PhCH$_2$CH$_2$-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] (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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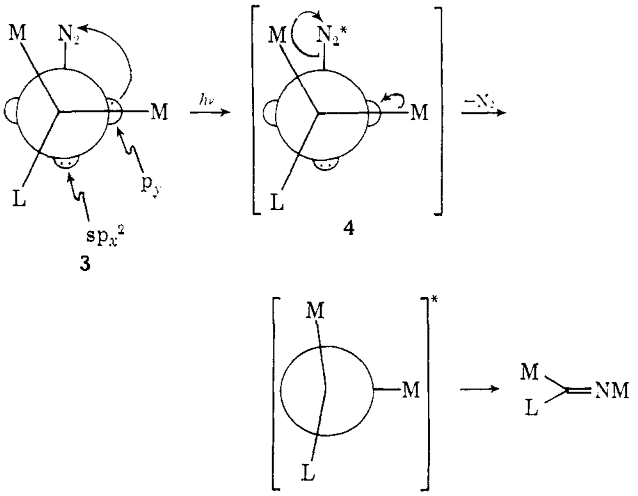

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(1) (a) L. Horner and A. Christmann, *Angew. Chem.*, **75**, 707 (1963); (b) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 149 (1964); (c) F.D. Lewis and W. H. Saunders, Jr., in "Nitrenes," W. Lwowski, Ed., Interscience Publishers, New York, N. Y., 1970, p 47.

(2) (a) W. H. Saunders, Jr., and E. A. Caress, *J. Amer. Chem. Soc.*, **86**, 861 (1964); (b) F. D. Lewis and W. H. Saunders, *ibid.*, **90**, 7031 (1968).

(3) R. A. Abramovitch and E. P. Kyba, *Chem. Commun.*, 265 (1969).

(4) R. M. Moriarity and R. C. Reardon, *Tetrahedron*, **26**, 1379 (1970).

(5) R. A. Abramovitch and E. P. Kyba in "The Chemistry of the Azido Group," S. Patai, Ed., Wiley, London, in press.

(6) W. D. Closson and H. B. Gray, *J. Amer. Chem. Soc.*, **85**, 290 (1963).

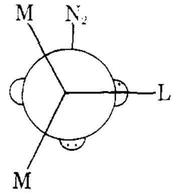
(7) Although not completely analogous, MO calculations of phenyl azide show that in the π–π^* excited state the α-nitrogen atom is electron deficient relative to the ground state.[8]

(8) A. Reiser and R. Marley, *Trans. Faraday Soc.*, **64**, 1806 (1968).

(9) The importance of orbital orientations in 1,2 shifts in carbonium ions has been emphasized recently.[10]

(10) D. M. Brouwer and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, **89**, 211 (1970).

The observed migration ratios can be accounted for if it is assumed that the most important steric interaction is between the large group L (*e.g.*, phenyl) and the azide N_2, so that conformation **3** would be more populated than **5** and the medium group M (*e.g.*, methyl) would have the suitable orientation for preferential migration **4**. If the correct preferred ground-state conformations are used, this theory will predict all the previous results[4] as well. This would also explain why, in the photolysis of several para-substituted triarylmethyl azides, both possible imines are obtained in statistical amounts,[2a] as the para substituent would not affect the ground-state conformation of the azide, while an *o*-phenyl group has an appreciable influence on the migration aptitude (Table I).



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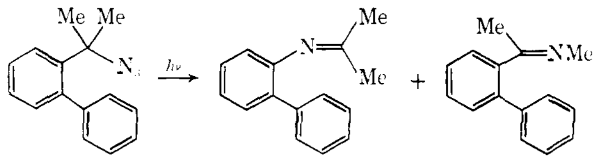
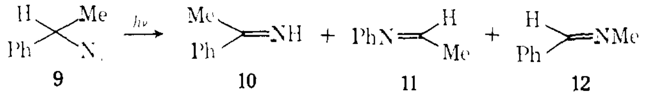


6 7 8

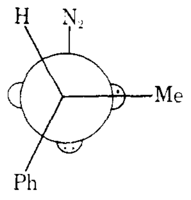
The primary importance of the ground-state conformation has been established conclusively by studying the influence of temperature upon the migration aptitudes in the direct photolysis of **6** (Table II) and of α-methylbenzyl azide (**9**) (Table III). The former gives two products, **7** and **8**, at low conversions,[11] while the latter gives the imines **10**, **11**, and **12**.



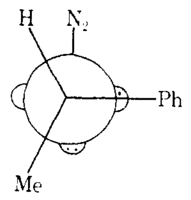
9 10 11 12

Thus, both sets of reactions approach a statistical distribution of migratory aptitudes as the temperature is raised, which is expected if the higher energy conformations are more populated, or, conversely, if the more stable conformation predominates at low temperatures. This clearly eliminates the highly reactive free nitrene intermediate as a contender, since the latter should be cylindrically symmetrical and have no conformational preference. If the relevant photoexcited state of the azide is indeed the $\pi_y\pi_z^*$ then the conformations of **9** which would explain the results would be **9a**, **9b**, **9c**, and **9b*** with the order of stability **9a** > **9b** ≃ **9c**.

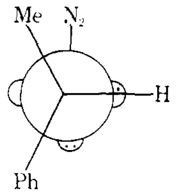
The results could also perhaps be explained if the photoexcited state were n–π*. In this case, the partially vacant orbital would be the sp_z^2 which is filled in the ground state, and to account for Me : Ph > 1 in 2-phenyl-2-propyl azide and in **9**, say, it would be necessary to postulate a repulsive interaction between the phenyl group and the sp_z^2 lone pair of electrons in the ground state, but not between methyl and lone pair, so that **9b** would be more stable than **9a**. Trans migration could then occur as in **9b***. There is no evidence at the moment, however, that an n → π* transition is involved. Photolyses have been carried out with light of wavelength >250 nm and the band at 216 nm is thought to be the n → π* while that at 285 nm is the π → π*. It is, of course, conceivable that tailing of the n → π* band could occur above 250 nm and give rise to the observed chemistry but there are presently no data to support this.



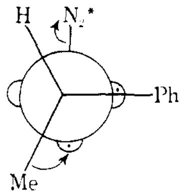
9a



9b



9c



9b*

Table II. Photolysis of **6** at Various Temperatures[a]

Temp, °C	Me[b]	2-Biphenylyl[b]	2-Biphenylyl–Me[c]
−117[d]	64.6	35.4	0.55
22[e]	59.1	40.9	0.69
101[f]	56.9	43.1	0.76

[a] Solutions *ca.* 0.02 *M* in azide used. [b] For synthesis of imines, see E. P. Kyba, *Org. Prep. Proc.*, **2**, 149 (1970). [c] Corrected for statistical preference for methyl migration. Values given are an average of duplicate runs at different conversions. Reproducibility was better than ±0.01. [d] Pentane solution. [e] Hexane solution. [f] Boiling methylcyclohexane solution. Azide does not undergo thermolysis at that temperature.

Table III. Photolysis of **9** at Various Temperatures[a]

	Percentage migration		
Temp, °C	H (**10**)	Ph (**11**)	Me (**12**)
−117	25.0	25.1	49.9
−77	26.2	26.9	47.0
22	29.0	29.2	41.8
101	31.1	31.4	37.7

[a] Solutions *ca.* 0.08 *M* in azide. Reproducibility of direct glc analysis better than 1%. Low conversion experiments were necessary since the products of both H and Ph migration decomposed at high conversions. The Me migration product was stable.

Acknowledgments. Support for this work by the National Science Foundation (GP-8869) is gratefully acknowledged.

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Received November 23, 1970

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(11) **7** cyclizes photolytically to 6,6-dimethyl-5,6-dihydrophenanthridine[3] but does so much more slowly than the imine is formed, so that at low conversions negligible amounts of cyclization products are formed.