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THE DIRECT AND PHOTOSENSITIZED DECOMPOSITION OF ALKYL AZIDES

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Abstract—The products of photolysis of n-butyl, n-amyl, 4-heptyl, 2-phenylethyl, 3-phenylpropyl, 4-phenylbutyl, phenylmethyl, 1-phenylbutyl, 1,1-diphenylethyl, and cyclohexyl azides were determined. Reactions were carried out to 5% completion in 0·10 molar benzene solution. The primary products of reaction are nitrogen and imines derived from hydrogen, alkyl or aryl migration to nitrogen. Corrected for the statistical factor the migratory order is H:R, 5:1; ϕ:H, 1:1; ϕ:R, 1:1. For cyclohexyl azide only α-hydrogen migration occurs.

The rate of nitrogen evolution was essentially the same for all the azides studied. The product distribution is unaffected by the presence of oxygen. Efficient photosensitization was achieved using chrysene and an appropriate filter system. The product ratios were unchanged in the photosensitized decomposition compared to the direct photolysis.

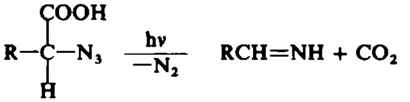
The results of this study are explained in terms of very shortlived singlet and triplet electronically excited azides. Evidence is summarized in favor of a closely synchronous migration of the α-substituent with the departure of molecular nitrogen from the excited azide. Conformational factors operative in the ground states of the alkyl azides may determine the migratory ratios and this possibility is discussed and evaluated.

ORGANIC azides in general decompose either thermolytically or photolytically *via* loss of molecular nitrogen to yield products formally derived from a nitrene radical. Variations in the organic azide have led to synthetically and theoretically valuable results. Less studied and more complex is the photochemical decomposition of alkyl azides.

Some areas of major uncertainty surround the photochemical decomposition of alkyl azides. For example, the question exists as to whether a discrete intermediary alkyl nitrene occurs in any of the photolyses reported thus far. The spin multiplicity of the alkyl nitrene or nitrenoid intermediate is not clearly established.*[3]

Earlier work has shown that the principal pathways for the photodecomposition involve the α-substituents either in migration to nitrogen[4a–i] or fragmentative cleavage.[5]

$$RCH_2{-}N_3 \xrightarrow[-N_2]{h\nu} RCH{=}NH + CH_2{=}N{-}R \qquad (5b)$$



$$R{-}\overset{COOH}{\underset{H}{C}}{-}N_3 \xrightarrow[-N_2]{h\nu} RCH{=}NH + CO_2 \qquad (5b)$$

$$R\overset{OH}{C}H{-}\overset{N_3}{C}HR \xrightarrow[-N_2]{h\nu} RCH{=}O + RCH{=}NH \qquad (6)$$

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* This does not refer to ESR[3] studies in solid matrices at 4°K. In these cases signals attributable to alkyl nitrenes in the triplet ground state have been reported.

In the present study we sought to gain information about the transition state and intermediates in the photodecomposition of alkyl azides by means of three methods. First, by using triplet photosersitization we hoped to generate a photoexcited triplet alkyl azide* and a triplet nitrene intermediate. Comparison of product distribution in the direct and photosensitized decompositions could yield information concerning the question of whether a singlet or triplet nitrene is involved in the direct photolysis.

Second, by sufficient variation in the structure of the alkyl azides one could relate either rate of nitrogen evolution or composition of reaction products to conformational factors, especially those prevailing at the carbon atom adjacent to the azido group.

Third, by systematic variation of the substituent at he α-carbon atom through hydrogen, alkyl, and aryl, and by determining migratory ratios in the imino product, one could possibly estimate the importance of bridging of the α-substituent in the transition state for loss of nitrogen.

RESULTS AND DISCUSSION

In order to minimize the possibility of formation of secondary reaction products photolyses were carried out to 5% completion.† Carbonyl products from imines, resulting from α-group migration, were isolated as 2,4-DNP derivatives and separated by dry column chromatography. Good reproducibility was achieved using this method.‡

For the first five azides listed in Table 1 one sees a remarkable constancy for the preference of hydrogen migration over alkyl group migration to nitrogen. The presence of a phenyl ring on the alkyl chain does not affect the ratio provided it is not in the α-position. In the case of 4-heptyl azide (**6**) the structural situation is reversed, for now two alkyl groups are available for migration to nitrogen in contrast to the previous five entries. Hydrogen migrated in preference to alkyl, but alkyl is about twice as competitive as might be expected from the prior examples (entries **1**–**5**). In the case of phenylmethyl azide (**8**) the phenyl : hydrogen ratio is unity. 1-Azidophenylbutane (**9**) presents the situation in which one of each; namely hydrogen, alkyl, and phenyl, is available for migration. Alkyl and phenyl group migration is equal and twice as great as hydrogen migration. Finally, in the case of cyclohexyl azide (**7**) only hydrogen migration occurs.

The point emerges from these data that a significant degree of selectivity occurs in the product forming step. This contrasts with the lack of selectivity observed in the photochemical decomposition of triarylmethyl azides both in the direct[4a] and photosensitized[4c] decompositions. Neglecting for the moment the question of the electronic spin multiplicity of the azide precursor, this selectivity is not at all expected if one assumes a high energy nitrene intermediate; in fact it would appear contradictory.

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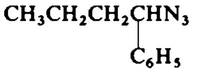
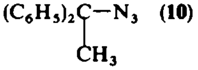
* In the case of triarylmethyl azides no change in the product distribution was observed in the photosensitized reaction relative to the direct photolytic decomposition.[4c]

† Selective photodecomposition of benzophenone methylimine was observed to occur in the photolysis of 1,1-diphenylethyl azide.[4a, b] Due to the photolability of the products in these reactions it is absolutely essential that any mechanistic discussion of products be based upon results from low conversions.

‡ This method[6] is strongly recommended for quantitative separation of 2,4-DNP derivatives because it clearly yields results of high reproducibility.

TABLE 1[a]. MIGRATORY RATIOS FOR HYDROGEN ALKYL AND PHENYL CORRECTED FOR THE STATISTICAL FACTOR

	Azide	H	R	C_6H_5
(1)	$CH_3CH_2CH_2CH_2N_3$ (1)[b]	5	1	
(2)	$CH_3CH_2CH_2CH_2CH_2N_3$ (2)	5	1	
(3)	$C_6H_5(CH_2)_4N_3$ (3)	5	1	
(4)	$C_6H_5(CH_2)_3N_3$ (4)	5	1	
(5)	$C_6H_5(CH_2)_2N_3$ (5)	5	1	
(6)	$(C_3H_7)_2CHN_3$ (6)[b]	5	2	
(7)	cyclohexylN_3 (7)	1		
(8)	$C_6H_5CH_2N_3$ (8)[b]	1		1
(9)	 $CH_3CH_2CH_2\underset{C_6H_5}{\underset{\mid}{C}}HN_3$ (9)[b]	1	2	2
(10)	 $(C_6H_5)_2\underset{CH_3}{\underset{\mid}{C}}{-}N_3$ (10)		1	1

[a] 5% completion of reaction for 0·10 M solution in C_6H_5.
[b] Photosensitized decomposition was studied.

In the alkyl azides under discussion that amount of electronic energy supplied upon excitation is around 100 kcal/mole while the bond dissociation energy of $RN{-}N_2$ is around 40–50 kcal/mole.[7, 8] Making the reasonable assumption that this excess electronic energy is rapidly converted into kinetic energy, it is clear that the excited azide molecule has energy in excess of that required for dissociation. Loss of molecular nitrogen offers a facile pathway for dissipation of a portion of this energy. The low energy requirement for cleavage of the N—N bond contributes to the short lifetime of the excited azide. If this lifetime is of the order of a few vibrations, i.e. ca. 10^{-11} sec, it is clear that no rotation in the molecule can occur prior to dissociation. Herein lies a possible rationalization of the observed migratory ratios. Assuming that the lifetime of the alkyl nitrene with respect to imine formation is less that 10^{-10} sec, rotational equilibration in the excited state may not occur before group migration to nitrogen. This is essentially equivalent to saying that the group migration from the α-C atom is concerted with nitrogen loss. Since the group *trans* to the departing nitrogen is the one which is stereoelectronically best situated for migration, a conformational analysis of the ground state of the alkyl azides should correlate the observed product ratios.

First, however, it is appropriate to offer some evidence for the lifetimes of the electronically excited alkyl azides and alkyl nitrenes. For the alkyl azides no fluorescence at 77° K was observed for pure solids[4b] and the quantum yield for decomposition of ethyl azide in solution is unity.[9] No quenching of azide by oxygen was observed and neither quenching by *cis*-piperylene nor its photoisomerization was observed.[4i] These two latter processes, however, would require a triplet excited from of the azide.

Several independent lines of evidence point to a very short-lived nitrene intermediate. First no bimolecular reaction of the alkyl nitrenes with the solvent benzene has been observed in the present study. Previous work indicated no more than 4% of these products.[4b, h] Photolysis of alkyl azides in isopropyl alcohol yielded no acetone by possible bimolecular photoreduction of an intermediary nitrene. Photolysis of alkyl azides as pure liquids or in solution yielded no azo compounds of alkanes derived from further photolytic decomposition of precursor azo alkanes. Finally the data listed in Table 2 indicates the essential insensitivity of the rate of decomposition of the alkyl azide to variation in structure.

TABLE 2. RELATIVE RATES OF NITROGEN EVOLUTION OF ALKYL AZIDES AT 25°

$R{-}N_3$	Rate Rel.
n-$C_4H_9N_3$	1
$\phi(CH_2)_4N_3$	0·96
$\phi(CH_2)_3N_3$	0·97
$\phi(CH_2)_2N_3$	0·89
ϕCH_2N_3	0·86
$C_3H_3CHCH_3N_3$	0·89
$C_6H_5N_3$	1·78

[a] Rate determined for 5% conversion.

The uniform absence of bimolecular reactions indicates that the rate constant for unimolecular rearrangement of the alkyl nitrene could be of the order of 10^6 sec^{-1}. Now if one accepts these approximate values for excited azide lifetime and rate constant for intramolecular rearrangement it follows that the conformation of the ground state is also the conformation of the transition state for rearrangement. Fig. 1 shows the geometric relationships between the migrating group and the incipient nitrenoid nitrogen (an angle of 115–120° for CN_1N_2 is assumed).[10, 11] The in-plane bending of the azido group, which has a small energy does not affect the argument because it simply offers another pathway for populating conformational minima.[12]

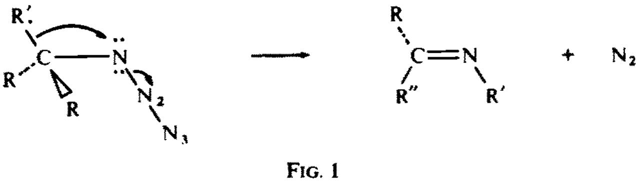


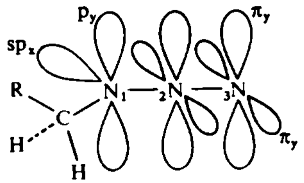
FIG. 1

A typical alkyl azide is stabilized by resonance contributors A and B.[13]

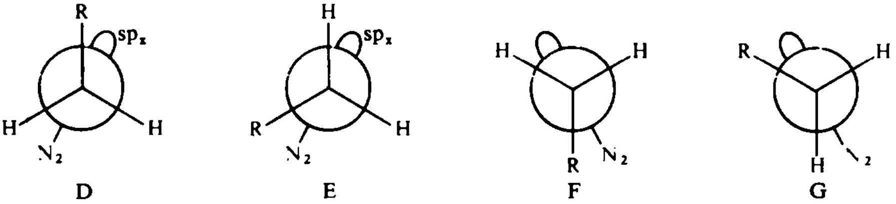
$$RCH_2{-}\overset{\ominus}{\underline{N}}{-}\overset{\oplus}{N}{\equiv}N| \longleftrightarrow RCH_2{-}\underline{N}{=}\overset{\oplus}{N}{=}\overset{\ominus}{\underline{N}}$$

A B

In terms of a representation involving overlap of atomic orbitals, linear structure C indicates interaction of the electron pair in py at N_1 with the π system of N_2 and N_3. The other electron pair at N_1 is localized in the $SP_{\overline{X}}$ orbital.[14]



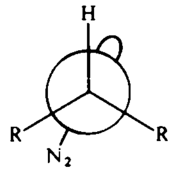
Among the conformations D—G for the alkyl azide it is reasonable to assume that the line pair is smaller than N_2 and the lone pair —H interaction is smaller than the lone pair alkyl group interaction. Between conformations D and E it appears reasonable that eclipsing of the alkyl group R with the lone pair would be a more serious steric interaction than one involving eclipsing of hydrogen with the lone pair. Therefore, conformation E would contribute more to the ground state rotational equilibrium than D. If no rotational equilibration occurs in going to the transition state for nitrogen loss and group migration the group which does in fact migrate is in effect determined by relative conformational stabilities of the ground state rotational isomers. The barrier height for rotation about CN_1 bond should not be very great. The torsional barrier in methyl isothiocyanate is 0·34 kcal/mole[15] while that for methyl isocyanate[16] is only 0·05 kcal/mole.



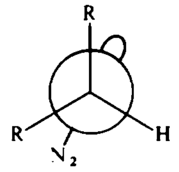
The viewpoint developed above, in effect, obviates the question of a discrete nitrene. The transition state proposed involves α-group to nitrogen as the molecule of nitrogen begins to leave. Of course, the reason for bridging in this system is based upon the short lifetime of intermediates, and it is fundamentally different from the related phenomenon in systems where bridging lowers the energy of activation for a reaction step.

On the basis of the conformational interpretation of product distribution one sees immediately that the migratory preference in the triarylmethyl azide photodecomposition, irrespective of *p*-substituent, must be unity, for the three conformations of the ground state must be equally populated because of symmetry.

Turning now to the question of the relationship of ground state conformation and migratory aptitude in alkyl azides of structure RCH_2N_3 it is not unreasonable that the ratio of D:E might be 1:5. Assuming that the transition state for migration also has the conformation the 5:1 H:R migratory ratio occurs.

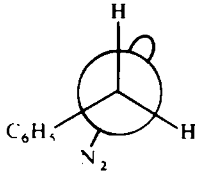


H

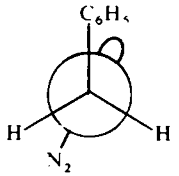


I

Again making the reasonable assumption that the lone pair —H interaction is less than the lone pair —R interaction and both are less than the corresponding interactions involving N_2, then conformation H is clearly the more stable. The 5:2 H:R migratory ratio agrees with a conformational population of H:I = 5:2.

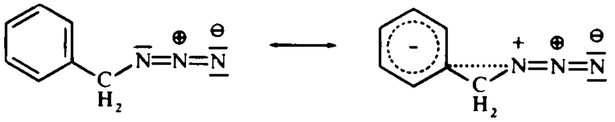


J



K

The migratory aptitude of the phenyl group is anomalously large if one considers that conformation J should be at least as favored with respect to K as it is in the case where the phenyl is replaced by alkyl, namely in the system RCH_2N_3, where R = alkyl. It may be that the ground state of the azide is stabilized by homoconjugative structures. This would favor conformation K.



Photosensitized decomposition of the alkyl azides could be achieved using a filter system which excluded all radiation below 340 mμ and allowed about 65% transmission above 360 mμ. Chrysene (Et = 57 kcal/mole) in benzene was used as the photosensitizer. Considerable difficulty was encountered in finding a system in which direct photolysis of the alkyl azide could be substantially suppressed. Under the above filter conditions chrysene caused a greater than 5-fold increase in rate of decomposition relative to the reaction in which only light > 340 mμ was admitted in the absence of photosensitizers.*

For compounds **1**, **6**, **8** and **9** no difference in the migratory ratios was observed in the triplet photosensitized reaction. This result is in agreement with the occurrence of a triplet azide in the direct photolysis although it does not require this circumstance. For example the mode of decomposition of singlet and triplet azides could be fortuitously the same. The lifetime of the triplet azide with respect to nitrogen loss and migration might be comparably short to that of the singlet azide.

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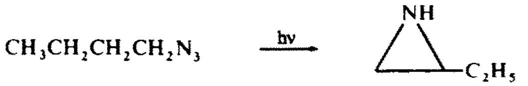
* Chrysene may cause single rather than triplet photosensitization. In unpublished work F. D. Lewis and J. C. Dalton, Columbia University, have shown that hexyl azide is a very efficient quencher of chrysene and other hydrocarbons and that singlet quenching leads to azide decomposition.

One final possibility which must be considered is that the rate of intersystem crossing from singlet azide to triplet azide is fast relative to decomposition. The present results cannot exclude this process. Lack of definite knowledge of the triplet state energy of the alkyl azide makes speculation on this process subject to uncertainties.

An obvious alternative to the above description of the photolysis of alkyl azides would involve photodissociation to yield a free discrete nitrene. Because of the tetrahedral symmetry of this species no conformational preference is possible, nor can migration be based on such a stereochemical factor. Migration would be determined by an intersection of the potential energy surfaces for the migratory processes with those for the excited states of the azide (either electronic or vibrational), or by the relative activation energies for the processes from the RN intermediate. Presumably the activation energies would be surmounted by available thermal energy.

A further possible pathway for imine formation involving the discrete nitrene is insertion into the β-carbon to yield an ethylenimine intermediate. This could be rejected, however, because 2-ethylaziridine, the intermediate which would be derived by this scheme from n-butyl azide, was not only stable under the photolytic conditions but also yielded methyl ethyl ketone in the work-up procedure. The latter compound was not found as a product of any of the photolyses performed in this study.



The most straightforward way of testing further the conformational basis for selectivity proposed above would be to study the gas phase photolysis and solution thermolysis of alkyl azides. Both experiments are complicated by the instability of the imino products.

EXPERIMENTAL

Synthesis of compounds. The method of preparation and physical properties of the alkyl azides used in the study are presented in Table 3. The method of Henkel and Weygand[17] using the alkyl bromide and sodium azide in aq MeOH (A) and the method of Smith and Brown[18] using aq EtOH and sodium azide (B) were employed.

General procedure for irradiation and product analysis

A Hanau medium pressure Hg lamp surrounded by a Pyrex water-cooled heat exchanger in a Pyrex reaction vessel equipped with a magnetic stirrer was used in the photolyses.

Approximately 0·12 mole of the azide in 200 ml dry, distilled benzene was added to the reaction vessel. Ultrapure N_2 was then introduced through a fine fritted disc at the bottom of the reaction vessel and passed from the vessel through a 2 mm ID exit port located above the surface of the soln. For experiments in which only an approximate percent decomposition of azide was required, N_2 evolution was determined by exiting the gas through one end of a 12–18 in. length of 1 mm ID tygon tubing attached to an inverted, water-filled gas buret. For kinetic measurements, a specially-constructed pressure control apparatus was used to determine quantitatively the amount of evolved N_2.

In chrysene-sensitized decompositions, a Corning 0–52 cut-off filter blank was placed between the Hg arc and the reaction vessel so that the filter was just touching the Pyrex heat exchanger and the reaction vessel. The filter excluded all radiation below 340 mμ and allowed approximately 65% transmission at 360 mμ. Control reactions indicated that the sensitized reactions were at least 5 times faster than unsensitized reactions under these conditions. In a typical photolysis, the work-up procedure was as follows: After photolysis resulted in 5% conversion of azide, as determined by N_2 evolution, a 50 ml aliquot was transferred

TABLE 3. ALKYL AZIDES

R—N$_3$	Method	Physical properties
n-Butyl (1)	A	n_D^{20}1·4102; 71° (225 mm)
		lit n_D^{22}1·4193; 65–69° (220 mm)[20]
n-Amyl (2)	A	n_D^{23}1·4185; 73–74° (100 mm)
		n_D^{20}1·4266; 63·5° (100 mm)[20]
4-Phenylbutyl (3)	B	n_D^{27}1·5200; 116–120° (5 mm)
		lit n_D^{27}1·5188; 114–116° (4 mm)[4b]
3-Phenylpropyl (4)	B	n_D^{26}1·5258; 76–78° (3 mm)
2-Phenylethyl (5)	B	n_D^{26}1·5312; 126° (20 mm)
		lit n_D^{26}1·5302; 68° (0·5 mm)[21]
4-Heptyl (6)	B	n_D^{23}1·4370; 78–80° (200 mm)
Cyclohexyl (7)	B	n_D^{23}1·4760; 66–67° (22 mm)
		n_D^{20}1·4693; 72° (30 mm)[20]
Phenylmethyl (8)	A	106–108° (42 mm)
1-Phenylbutyl (9)	B	n_D^{26}1·5141; 85–88° (3·5 mm)
1,1-Diphenylethyl (10)	B	n_D^{23}1·5000; 81–82° (3·0 mm)
Phenyl azide	B	49° (5 mm)
		lit 50° (5 mm)[22]

2-*Ethyl aziridine* was prepared according to the method of Campbell *et al.*[23] and had n_D^{23}1·4193, b.p. 66–69° (200 mm) lit, 71° (225 mm), n_D^{20}1·4192.

2,4-*Dinitrophenylhydrazones* were prepared according to the method of Shriner *et al.*[24]

TABLE 4. 2,4-DINITROPHENYLHYDRAZONE R_B VALUES

Compound	R_B	m.p.
CH_2O	0·52	166
$CH_3CH_2CH_2CHO$	0·79	122
$CH_3COCH_2CH_3$	0·70	129
$CH_3CH_2CH_2CH_2COC_6H_5$	1·18	
$CH_3COC_6H_5$	0·98	250
$C_6H_5COC_6H_5$	1·16	239
$C_6H_5CH{=}O$	0·92	237
$CH_3CH_2CH_2COCH_2CH_2CH_3$	1·11	74°

$$R_B = \frac{\text{distance traveled by carbonyl compound}}{\text{distance traveled by } [p\text{-}(CH_3)_2NC_6H_4]_2N_2}$$

Solvent system: 3:1 C_6H_5: light petroleum (30–60°).

to a 500 ml 3-necked round-bottom flask fitted with a stirrer. To this was added a 200-ml portion of a filtered soln (2NHCl) of 2,4-dinitrophenylhydrazine. The resulting two-phase system was stirred at high speed for 3 hr. The benzene layer was then separated, the aqueous layer was washed once with a 50 ml portion benzene, the benzene extracts combined, dried, filtered and concentrated on a rotary evaporator (water aspirator) at 35–50°. The resultant residue was dissolved in the minimum amount of solvent (chloroform or benzene) and the mixture subjected to dry column chromatography. This was done by adding the mixture to the top of a 3′ × 1 in. ID glass column containing 300 g of silica gel. The silica gel had been previously mixed with 15% by weight of a 3:1 mixture of benzene: light petroleum (30–60°). The column was then developed by allowing the same solvent mixture to descend through the column. Unreacted azide, 2,4-dinitrophenylhydrazone derivatives, and chrysene in the case of sensitized reactions, were eluted from the column and collected in fractions. The solvent was evaporated and the fractions weighed. Identity of the individual fractions was determined by comparison of their TLC R_B values with those of the authentic

2,4-DNP derivatives. Further identification of the components was obtained by combining the middle fractions of each component (i.e., of each 2,4-DNP derivative) as determined by TLC and carrying out m.p. and mixed m.p. determinations on each component.

In some photolyses reproducibility of reactions was determined by separating the 2,4-DNP derivatives from two photolyses of the same azide by means of preparative TLC using 3:1 benzene: light petroleum (30–60°). The derivatives were separately transferred to fritted disc filter funnels, washed out with chloroform and the filtrates transferred to volumetric flasks. Comparison of the UV absorptions of the components of one photolysis with those of another photolysis was employed to determine reproducibility.

A 1–2 ml aliquot of the photolysate was removed and subjected to TLC and VPC analyses. A BuOH–AcOH–water (80/20/1p: v/v/v) solvent system and ninhydrin spray was used for TLC analyses. VPC analyses were carried out using an F&M Research Chromatograph 5150 with column A (6' × $\frac{1}{16}$ in., 10% UC W98, 80/100 mesh S) or a Glowall Chromolab 310 with column B (6' × $\frac{1}{4}$ in., 10% Carbowax 20 M, 60/80 mesh Chromosorb). Authentic samples were used for comparison in both TLC and VPC analyses.

The remainder of the photolysate was then irradiated to >90% conversion or until N_2 evolution had ceased. TLC and VPC analyses identical with those described for an aliquot of the 5% conversion product were performed.

Kinetic determination of nitrogen evolution

A constant pressure–variable volume system was constructed in order to determine the volume of N_2 evolved. The system was a modification of that described by Baldwin.[20] Connection from the gas exit port of the reaction vessel to the pressure sensing apparatus, was well as all connections within the apparatus, were made with 1-mm capillary tubing. The tubing from the reaction vessel connected with a glass T-joint. One route led to a U-tube containing an aqueous suspension of Sudan Black dye. A photocell was located just below the meniscus of the suspension. The other route led to the top of a 50 ml buret filled with light machine oil. A 50 ml syringe was attached to the lower end of the buret and was clamped to a constant-speed syringe drive apparatus. The syringe drive motor was a Warren Telechron C-2 synchronous motor, 150 volts, 60 cycles, 4 rpm, 6 watts.

As N_2 was evolved from a reaction, a slight increase in the pressure of the closed system was detected by the photocell as the meniscus in the U-tube was depressed. The photocell was thus activated, and in turn activated the syringe-drive apparatus which withdrew enough liquid in the buret to maintain a constant pressure in the system. Periodic readings taken directly from the buret were recorded as the volume of N_2 evolved.[21]

Photolysis of n-butyl azide. A soln of 2 g (0·02 mole) of n-butyl azide in 200 ml benzene was irradiated under the conditions outlined in the general photolytic procedure. After 70 min 5% reaction had occurred as indicated by N_2 evolution. A 50-ml aliquot of the photolysate was transferred to a 500 ml, 3-necked round-bottom flask fitted with a stirrer. To this was added a 200 ml portion of a 0·02 M soln (2NHCl) of 2,4-DNP as described in the general procedure. The 2-phase system was stirred at high speed for 4 hr. The benzene layer was then separated, the aqueous layer washed once with a 50 ml portion of benzene, the benzene extracts combined, filtered and concentrated in a rotary evaporator. The residue (0·6 g) was dissolved in the minimum amount of solvent ($CHCl_3$) and the mixture subjected to dry column chromatography, using 300 g silica gel. Unreacted azide and 2,4-DNP derivatives were eluted and collected in fractions. The solvent was evaporated and the fractions weighed. Butyraldehyde 2,4-DNP (60 mg, 0·24 mmole) and formaldehyde 2,4-DNP (5 mg, 0·02 mmole) were obtained. This accounts for the converted azide within experimental error and represents a ratio of hydrogen migration *vs* alkyl migration of greater than 10 to 1.

A 1–2 ml aliquot of the original photolysate was removed, concentrated and subjected to TLC and VPC analyses. Using a BuOH–AcOH–water (80/20/10: v/v/v) solvent system and a 2% ninhydrin spray soln as developer, authentic samples of pyrrolidine, N-n-butylaniline, n-butylamine and propylamine were well separated. TLC analysis indicated the absence of any of these compounds in the photolysate. VPC analysis of a mixture of these amines (ca. 1/1/1/1: v/v/v/v) on an F&M 5750 Research Chromatograph showed four major peaks using a hydrogen flame detector and column A (ambient temp; injection port, 150°). VPC analysis of the photolysis under the same conditions indicated the absence of any of the four amines in the photolysate.

The remainder (ca. 150 ml) of the photolysate was then irradiated until the soln no longer evolved N_2 (>90% conversion). TLC and VPC analyses indentical with those described for an aliquot of the 5% conversion photolysate were negative for the presence of the 4 amines.

Reproducibility of this reaction was determined by carrying out the photolysis of n-butyl azide in essentially the same manner as that described for the 5% conversion of n-butyl azide. Workup of a 50 ml aliquot of the photolysate with 2,4-dinitrophenylhydrazone was also carried out in the same manner. The concentrated 2,4-dinitrophenylhydrazone mixture from each photolysis was subjected to preparative TLC using 3:1 benzene:light petroleum (30–60°). The derivatives were separately transferred to fritted disc filter funnels and each washed into a separate volumetric flask with chloroform. The UV absorption of the three formaldehyde 2,4-DNP derivatives was measured at 348 mμ (λ_{max}). The relative concentrations of butyraldehyde to formaldehyde for a given photolysis were determined by the relationship

$$\frac{a_1}{a_2} = \frac{\varepsilon_1 c_1}{\varepsilon_2 \varepsilon_2}$$

so that

$$\frac{c_1}{c_2} = \frac{a_1 \varepsilon_2}{a_2 \varepsilon_1}$$

For one photolysis $c_1/c_2 = 9{\cdot}7$, for the second $c_1/c_2 = 10{\cdot}5$ and for the third $c_1/c_2 = 10{\cdot}1$.

Photolysis of n-butyl azide in the presence of oxygen. A soln of 2 g (0·02 mole) of n-butyl azide in 200 ml benzene was irradiated for 70 min during which time O_2 was passed through the system. Separation of the 2,4-DNP mixture by preparative TLC followed by UV absorption measurements of the formaldehyde and butyraldehyde derivatives thereby obtained, indicated the ratio of butyraldehyde to formaldehyde to be greater than 10 to 1.

In another experiment, O_2 was bubbled into a soln of 2 g (0·02 mole) of n-butyl azide in 200 ml dry, distilled benzene only prior to photolysis (for 20–30 min). The soln was then irradiated for 70 min and worked up in the same manner as that described for the 5% conversion of n-butyl azide. Separation of the 2,4-DNP mixture by preparative TLC, followed by UV absorption measurements of the formaldehyde and butyraldehyde derivatives, indicated the ratio of butyraldehyde to formaldehyde was greater than 10 to 1.

4-Azidoheptane. 2·82 g (0·02 mole) in 200 ml benzene was irradiated in the same way as that described for the 5% conversion of n-butyl azide except that conversion was carried out only to the extent of 4%. The usual 2,4-dinitrophenylhydrazine workup followed by dry column chromatography of the resulting 2,4-DNP mixture gave 16 mg (0·06 mmole) 4-heptanone 2,4-DNP and 22 mg (0·09 mmole) butyraldehyde 2,4-DNP. This accounts for about 95% of converted azide and represents a preference for hydrogen migration *vs* alkyl migration by a ratio of 5 to 4.

A 1–2 ml aliquot of the photolysate, subjected to the usual TLC and VPC (column A, 100°) analysis, indicated that no 2-n-butylpyrrolidine was present by comparison with an authentic sample.

The remainder of the photolysate was then irradiated until the soln no longer evolved N_2 (>90% conversion) and the TLC and VPC analyses repeated. These analyses indicated that no 2-n-butylpyrrolidine was present by comparison with an authentic sample.

2-Phenylethyl azide. 2·94 g (0·02 mole) in 200 ml benzene was photolyzed to 5% conversion in 15 min in the manner described in the general procedure. Workup of a 50 ml aliquot of the photolysate with 2,4-dinitrophenylhydrazine, followed by separation of the 2,4-DNP mixture by dry column chromatography, was carried out in the usual manner and gave 55 mg (0·18 mmole) 2-phenylacetaldehyde 2,4-DNP and 4 mg (0·02 mmole) formaldehyde 2,4-DNP. This accounts for 80% of the converted azide and represents a preference for hydrogen migration vs alkyl migration of 9 to 1.

3-Phenylethyl azide. 3·22 g (0·02 mole) in 200 ml benzene was irradiated to 5% conversion (80 min) in a manner described in the general procedure. Workup of a 50 ml aliquot of the photolysate with 2,4-dinitrophenylhydrazine, followed by separation of the 2,4-DNP mixture by dry column chromatography, was carried out in the usual manner and gave 66 mg (0·21 mmole) 3-phenylpropionaldehyde 2,4-DNP and 6 mg (0·03 mmole) formaldehyde 2,4-DNP. This accounts for greater than 90% of the converted azide and represents a preference for hydrogen migration *vs* alkyl migration of 7 to 1.

A 1–2 ml aliquot of the photolysate was subjected to the usual TLC and VPC analyses (column A, 100°). No tetrahydroquinoline could be detected by comparison with an authentic sample. The remainder of the photolysate was irradiated to about 40% conversion and the TLC and VPC analyses repeated. No tetrahydroquinoline could be detected.

4-Phenylbutyl azide. 3·50 g (0·02 mole) in 200 ml benzene was irradiated to 5% conversion (70 min) in the same manner as that described for the 5% conversion of n-butyl azide.

Workup of a 50 ml aliquot with 2,4-dinitrophenylhydrazine, followed by separation of the 2,4-DNP mixture by preparative TLC, was carried out in the usual manner. UV absorption measurements of the 2,4-DNP derivatives indicated the ratio of hydrogen migration *vs* alkyl migration was about 10 to 1.

The usual TLC and VPC analyses of the photolysate after 5 % conversion, were negative for the presence of 2-phenylpyrrolidine. However, after irradiation to >90 % conversion, both TLC and VPC analyses of the photolysate (after concentration of the residue to about 25 ml) indicated that small amounts of 1–5 % of 2-phenylpyrrolidine were present. About 10 ml of the concentrate were added to 25 ml of a saturated soln [95 % (Etow)] of picric acid and the mixture refrigerated overnight. No ppt was observed.

Phenylmethyl azide. 2·66 g (0·02 mole) in 200 ml benzene was irradiated to 5 % conversion (80 min) as above. Workup of a 50 ml aliquot with 2,4-dinitrophenylhydrazine, followed by separation of the 2,4-DNP mixture by dry column chromatography, was carried out in the usual manner and gave 16 mg (0·05 mmole) butyrophenone 2,4-DNP, 30 mg (0·11 mmole) benzaldehyde 2,4-DNP and 22 mg (0·08 mmole) butyraldehyde 2,4-DNP which represents a ratio of alkyl *vs* phenyl vs hydrogen migration of 2:1·6:1. This accounts for >90 % of the converted azide.

The usual TLC and VPC analyses of the photolysate after conversion to 5 % and to 90 % were negative for the presence of 2-phenylpyrrolidine by comparison with an authentic sample.

2-*Azidopentane.* 2·26 g (0·02 mole) was irradiated to 5 % conversion (75 min) as described above. TLC of the 2,4-DNP mixture obtained in the usual manner indicated that 2-pentane 2,4-DNP and butyraldehyde 2,4-DNP were not separable.

Diphenylmethyl azide. 4·18 g (0·02 mole) was irradiated in the same manner as that used for 5 % conversion of n-butyl azide. No N_2 evolution was detected after several hr. Therefore, the Pyrex insert at the mouth of the reaction vessel was replaced by a quartz insert of the same dimensions with a 250-watt, medium press Hg arc (Westinghouse). The insert was double-walled and was equipped with a water inlet-outlet system to serve as a heat exchanger. Conversion to 5 % required 4–5 hr. Workup of a 50 ml aliquot of the photolysate with 2,4-dinitrophenylhydrazine, followed by separation of the 2,4-DNP mixture by dry column chromatography, was carried out in the usual manner and gave 7 mg (0·02 mmole) benzophenone 2,4-DNP and 77 mg (0·3 mmole) benzaldehyde 2,4-DNP.

Diphenylethyl azide. 4·46 g (0·02 mole) was irradiated to 5 % conversion as described above for the 5 % conversion of n-butyl-azide. Workup of a 50 ml aliquot with 2,4-dinitrophenylhydrazine, followed by separation of the 2,4-DNP mixture by dry column chromatography, was carried out in the usual manner and gave acetophenone 2,4-DNP (75 mg, 0·25 mmole) and benzophenone 2,4-DNP (25 mg, 0·07 mmole) which accounts for quantitative conversion. This product distribution represents a preference for phenyl migration versus alkyl migration of 1·8 to 1.

Cyclohexyl azide. 2·50 g (0·02 mole) was irradiated to 5 % conversion. The usual 2,4-DNP workup and TLC analysis gave only cyclohexanone 2,4-DNP.

2-*Ethyl aziridine.* 0·1 g in 200 ml dry distilled benzene was irradiated for 3 hr. Workup of a 50 ml aliquot of the photolysate with 2,4-dinitrophenylhydrazone was carried out in the usual manner. TLC analysis of the resulting 2,4-DNP mixture indicated the formation of only methylethylketone 2,4-DNP.

Phenylmethyl azide. 2·66 g (0·02 mole) in 200 ml very pure isopropyl alcohol was irradiated to 5 % conversion based on N_2 evolution. A 1–2 ml aliquot of the photolysate was then removed and subjected to VPC analysis (injection port: 150°, column oven: 80°). No acetone was detected under instrument conditions (attenuation: 5, flow rate: 30 ml/min) which are appreciably sensitive to 1×10^{-3} molar soln of acetone (in isopropyl alcohol). This sensitivity was determined by VPC analysis of 1×10^{-3} molar test soln the composition of which represents oxidation of isopropyl alcohol to acetone by only 10 % of converted azide (5 % conversion based on azide). The photolysate was then irradiated to an additional 10 % conversion (total conversion: 15 %) and VPC analysis was negative for even trace amounts of acetone.

2-*Azidopentane.* 2·26 g (0·02 mole) in 200 ml very pure isopropyl alcohol was irradiated to 5 % conversion. A 1–2 ml aliquot of the photolysate was then removed and subjected to VPC analysis using column B (injection port: 150°, column oven: 80°). No acetone was detected under instrument conditions (attenuation: 5, flow rate: 30 ml/min) which are appreciably sensitive to 1×10^{-3} molar soln of acetone. The photolysate was then irradiated to an additional 10 % conversion (total conversion: 15 %) and VPC analysis was negative for even trace amounts of acetone.

n-Butyl azide and chrysene. A 100-watt Hanau medium press Hg-lamp surrounded by a Pyrex water-cooled heat exchanger was placed in a Pyrex reaction vessel. A Corning 0–52 cut-off filter was interposed between the Hg-lamp and the reaction vessel so that the filter was just touching the Pyrex heat exchanger and the reaction vessel. The filter excluded all radiation below 340 mμ and allowed approximately 65 % transmission at 360 mμ.

A soln of 2 g (0·02 mole) n-butyl azide and 0·4 g chrysene in 200 ml benzene was added to the Pyrex reaction vessel. Ultrapure N_2 was then introduced through a fine fritted disc in the bottom of the vessel. After purging for 20–30 min the N_2 flow was stopped, the N_2 inlet sealed tightly with a stopper (rubber), and the gas outlet connected to the pressure-control apparatus. A magnetic stirrer at the bottom of the reaction vessel kept the soln agitated during the photolysis.

The soln was then irradiated to 5% conversion based on N_2 evolution (105 min). A control reaction run under the same conditions without chrysene exhibited less than $\frac{1}{5}$th the amount of conversion as the sensitized photolysis, i.e., less than 1%, based on N_2 evolution for 105 min.

A 50 ml aliquot of the photolysate was transferred to a 500 ml, 3-necked, round-bottom flask fitted with a stirrer. To this was added a 200 ml portion of a saturated soln of 2,4-dinitrophenylhydrazone in 2N HCl which had been previously filtered. The two phase system was stirred at high speed for 3 hr. The benzene layer was then separated, the aqueous layer washed once with benzene (50 ml), the benzene extracts combined, dried, filtered and concentrated on a rotary evaporator (water aspirator) at 35–50°. The resultant residue (ca. 0·75) was dissolved in the minimum amount of solvent ($CHCl_3$) and the mixture subjected to dry column chromatography. This was done by adding the mixture to the top of a 3′ × 1 in. ID glass column containing 300 g of silica gel. The column was then developed by allowing the same solvent mixture to flow through the column in a descending manner. The 2,4-DNP derivatives, as well as chrysene and unreacted azide, were eluted and collected in fractions. The solvent was evaporated and the fractions weighed. The two derivatives obtained were butyraldehyde 2,4-DNP (60 mg, 0·24 mmole) and formaldehyde 2,4-DNP (5 mg, <0·03 mmole) which represents a ratio of hydrogen migration *vs* alkyl migration of greater than 10:1. Further identification of the components was obtained by combining the middle fractions of each component (determined by TLC using authentic 2,4-DNP derivatives) and carrying out m.p. and mixed m.p. determinations.

A 1–2 aliquot of the photolysate was removed, concentrated and subjected to TLC and VPC analyses. Using a BuOH–AcOH–water (80/20/10 : v/v/v) solvent system and a 2% ninhydrin spray soln as a developer, authentic samples of pyrrolidine, N-n-butylaniline, butylamine and propylamine were well separated. TLC analysis for the photolysate indicated the absence of any of these compounds in the photolysate. VPC analysis of a mixture of these same compounds (1/1/1/1 : v/v/v/v) on an F&M 5750 Research Chromatograph showed four major peaks using a hydrogen flame detector and column A (at ambient temp; injection port: 150°). VPC analysis of the photolysate under the same conditions indicated the absence of any of the four amines. The remainder (ca. 150 ml) of the photolysate was then irradiated until the soln no longer evolved N_2 (>90% conversion) and concentrated to about 10 ml. TLC and VPC analyses identical with those described for an aliquot of the 5% conversion photolysate were carried out and were negative for the presence of the four amines mentioned above.

4-*Azidoheptane and chrysene*. A soln of 2·82 g (0·02 mole) 4-azidoheptane and 0·4 g chrysene in 200 ml benzene was irradiated to 4% conversion (110 min) in the same manner described for n-butyl azide and chrysene. A control reaction run under exactly the same conditions, but without chrysene, exhibited less than $\frac{1}{7}$th the amount of conversion as sensitized photolysis, i.e., less than 0·7% based on N_2 evolution for 110 min.

A 50 ml aliquot of the photolysate was mixed with 200 ml of a saturated soln of 2,4-dinitrophenylhydrazine in 2N HCl at high speed stirring for 3 hr. The benzene layer was then separated, the aqueous layer washed once with a 50 ml portion benzene, the benzene extracts combined, dried, filtered and concentrated on a rotary evaporator at 35–50°. The resultant residue (ca. 0·7 g) was then dissolved in the minimum amount of benzene and the mixture subjected to dry column chromatography as described for n-butyl azide and chrysene. The unreacted azide and chrysene eluted first and were not separable. However, TLC of this mixture (3:1 benzene:light petroleum) confirmed that it consisted only of chrysene and azide by comparison with authentic samples. The 2,4-DNP derivatives were then eluted and collected in fractions. The solvent was evaporated and the fractions weighed. The two derivatives obtained were 4-heptanone 2,4-DNP (16 mg, 0·06 mmole) and n-butyraldehyde 2,4-DNP (22 mg, 0·09 mmole) which accounts for 75% of the converted azide and represents a ratio of hydrogen migration *vs* alkyl migration of 4:3.

A 1–2 ml aliquot of the photolysate was removed, concentrated and subjected to TLC and VPC analyses under exactly the same conditions as described for n-butyl azide and chrysene, i.e., TLC solvent mixture (BuOH–AcOH–water) and spray (ninhydrin) and VPC column (column A, ambient temp, injection port: 150°). Both of these analyses were negative for the presence of 2-n-butylaniline using an authentic sample as comparison. The remainder of the photolysate (ca. 150 ml) was then irradiated until the soln no longer evolved N_2 (>60% conversion) and the soln concentrated to about 10 ml. TLC and VPC analyses identical with those described for an aliquot of the 5% conversion photolysate were negative for the presence of 2-n-butylaniline.

Phenylmethyl azide and chrysene. A soln of 2·66 g (0·02 mole) phenylmethyl azide and 0·4 g chrysene in 200 ml benzene was irradiated to 5% conversion (117 min) as described for n-butyl azide and chrysene.

The 2,4-DNP residue (ca. 0·69 g) obtained by the procedure described above was dissolved in the minimum amount of benzene and the mixture subjected to dry column chromatography as described for n-butyl azide and chrysene using 3:1 benzene:light petroleum solvent. The two 2,4-DNP derivatives obtained were benzaldehyde 2,4-DNP (44 mg, 0·154 mmole) and formaldehyde (12 mg, 0·057 mmole) which accounts for 84% of converted azide and represents a ratio of hydrogen migration *vs* phenyl migration of 2·7 to 1.

In an essentially identical photolysis, 60 mg (0·210 mmole) benzaldehyde 2,4-DNP and 14 mg (0·035 mmole) formaldehyde 2,4-DNP were obtained by dry column chromatography. This yield accounts quantitatively for the converted azide (within experimental error) and represents a ratio of hydrogen migration to phenyl migration of 3:1.

1-*Azido*-1-*phenylbutane and chrysene.* A soln of 3·50 g (0·02 mole) 1-azido-1-phenylbutane, 0·4 g chrysene in 200 ml benzene was irradiated to 5% conversion (2·9 hr) as described for n-butyl azide and chrysene.

A 50 ml aliquot of the photolysate was mixed with 200 ml of a saturated 2,4-dinitrophenylhydrazine soln in 2N HCl as described. The residue (ca. 0·7 g) obtained was then dissolved in a minimum amount of benzene and the mixture subjected to dry column chromatography as described for n-butyl azide and chrysene using 3:1 benzene:light petroleum (30–60°) as solvent. The three 2,4-DNP derivatives obtained were benzaldehyde 2,4-DNP (29 mg, 0·11 mmole), n-butyraldehyde 2,4-DNP (22 mg, 0·08 mmole) and butyrophenone 2,4-DNP (8 mg, 0·03 mmole) which accounts for 90% of converted azide and represents a ratio of alkyl *vs* phenyl *vs* hydrogen migration of 2:16 < 1.

A 1–2 ml aliquot of the photolysate was removed and subjected to TLC and VPC analyses. TLC analysis (by comparison with an authentic sample of 2-phenyl pyrrolidine) indicated the absence of 2-phenylpyrrolidine using BuOH–AcOH–water (80/20/10: v/v/v) and ninhydrin spray. VPC analysis on a Glowal Chromolab 310 (column B, 100°, injection port 200°) was negative for 2-phenylpyrrolidine by comparison with an authentic sample. The remainder of the photolysate (ca. 150 ml) was irradiated until the soln no longer evolved N_2 (ca. 50% conversion). TLC and VPC analyses identical with those described for an aliquot of the 5% conversion photolysate were negative for the presence of 2-phenylpyrrolidine.

Neat phenylmethyl azide. A small (8 mm × 65 mm) Pyrex test tube was fixed within 15 mm of a 100-watt Hanau medium press Hg-arc surrounded by a Pyrex water-cooled heat exchanger. To the test tube were added 2 ml phenylmethyl azide and a few carborundum ebulators. The azide was photolysed until it no longer evolved N_2 (>8 hr). TLC analysis of the photolysate indicated the absence of bibenzyl (1,2-diphenylethane) by comparison with an authentic sample, using 20:1 light petroleum (30–60°): benzene solvent and iodine development.

Neat diphenylmethyl azide. A 1 cm quartz UV curette was placed approximately in the center of a Rayonnet UV apparatus (Model RPR 100) containing 13 low press Hg-arcs. To the test tube were added 3 ml diphenylmethyl azide and a few carborundum ebulators. The azide was photolysed for 20 hr after which no appreciable N_2 evolution could be detected and the liquid had turned a dark orange–brown. TLC analysis of the photolysate indicated the absence of sym-tetraphenylethane by comparison with an authentic sample using 20:1 light petroleum (30–60°): benzene solvent and iodine development.

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