

Table I. Photoconversion of **8A** to **15a** as a Function of Time^a

Time, h	% 8A	% 15a
0	100	0
2.0	80	8
4.0	61	23
6.0	49	33
8.0	36	35

^a Cyclohexane solution. See Experimental Section for details.

Table II. Photolysis of **8** as a Function of Temperature^a

temp, °C	yields, %		migratory ratio Ar/Me ^e
	8A	8B ≡ 8C	
-117 ^b	21.6	78.4	0.55 (0.49)
22 ^c	25.8	74.2	0.70
101 ^d	27.5	72.5	0.76 (0.74)

^a Yields given are for duplicate runs at different conversions of <50%. Mass balance was 96–100% in all cases. Approximately 0.02 M solutions of **8** were utilized. ^b Pentane solution. ^c Hexane solution. ^d Boiling methylcyclohexane solution. Azide **8** does not undergo thermolysis at this temperature. ^e Ar = 2-biphenyl. Ratios are corrected for the statistical preference of Me to migrate. Ratios were reproducible to ±0.01. Values in parentheses calculated, assuming ΔE_a at room temperature is correct; see Table V and text.

This azide (**10**) gave the poorest mass balance of all those investigated; at 65% disappearance of azide, only 87% of starting material could be accounted for as recovered **10** plus products.

Photolysis of 6, 7, and 11. Photolysis of **6** gave a phenyl/methyl migratory ratio of 0.75, this number being independent of the percentage conversion. In contrast, azide **7** gave a phenyl/methyl migratory ratio of 1.3,⁹ and this ratio was found to be essentially invariant with conversions from 1 to 40%, contrary to a report by another group.^{10,11}

Analysis of the products from the photolysis of **11** required an assumption concerning the gas chromatographic thermal response factor for imine **11A**, which we were unable to synthesize. Acetaldehyde and aniline condensed at low temperatures (-77 °C), as indicated by GLC monitoring, to give a peak which corresponded exactly in retention time to one of the products obtained from the photolysis of **11**. Attempts to isolate **11A**, however, led, by way of an exothermic polymerization, to an intractable material which was not further investigated. We established that, in dilute solution, **11A** appeared to be relatively stable, and its concentration did not change appreciably during the course of GLC analysis of azide photolysis mixtures (ca. 1 h), although during an extended period of time (>24 h) the loss of this component in the reaction mixture was appreciable. Because of these synthetic problems, we made the reasonable assumption that the thermal response factors of imines **11A** and **11B** were identical for the purposes of GLC analysis of the photolysis products of **11**. Table III summarizes the results of the photodecomposition of **11** over a large temperature range.

Photolysis of 12 and 13. The results of the photodecomposition at various temperatures of **12**, which gives rise to imines **12A** and **12B** (≡**12C**), are presented in Table IV. Photolysis of azide **13** at 10 °C gave imines **13A** (≡**13B**) and **13C** in yields of 67 and 33%, to give the *n*-Pr/H migratory ratio of 1.0. This ratio was essentially independent of extent conversion, ranging from 11 to 64%, and of temperature (down to -117 °C).

Discussion

Table V summarizes the migratory ratios derived above. Although most of the values are significantly different from unity, the range of migratory aptitudes nonetheless does not

Table III. Photolysis of **11** at Various Temperatures^a

Temp, °C	yields, %			migratory ratios Ph:Me:H ^b
	11A	11B	11C	
-117	25.1	49.9	25.0	0.50:1.0:0.50 (0.50:1.0:0.50)
-77	26.9	47.0	26.2	0.57:1.0:0.56 (0.58:1.0:0.58)
22	29.2	41.8	29.0	0.70:1.0:0.70
101	31.4	37.7	31.1	0.83:1.0:0.82 (0.75:1.0:0.75)

^a Solutions ca. 0.08 M in azide. Yields given are averages of at least two photolyses, carried to different partial conversions in the range of 7–24%, and then extrapolated to 100% conversion. Reproducibility between runs at the same temperature was better than 0.8%. Solvents used were: -117 °C, pentane; -77 °C, hexane; 23 °C, cyclohexane; 101 °C, boiling methylcyclohexane. ^b Values in parentheses calculated assuming ΔE_a at room temperature is correct; see Table V and text.

Table IV. Photolysis of **12** at Various Temperatures^a

Temp, °C	yields, %		migratory ratio <i>t</i> -Bu/Me ^b
	12A	12B ≡ 12C	
-117	53.1	46.9	2.26 (2.24)
-77	49.8	50.2	1.98 (1.90)
20	43.2	56.8	1.52

^a Pentane solutions ca. 0.08 M in azide. Yields given are averages of at least two photolyses, carried to different partial conversions in the range of 14–33%, and then extrapolated to 100% conversion. Reproducibility between runs at the same temperature was better than 0.5%. ^b Values in parentheses calculated, assuming ΔE_a at room temperature is correct; see Table V and text.

Table V. Migratory Aptitudes in the Photolysis of Some *sec*- and *tert*-Alkyl Azides^a

azide				ΔE_a , cal/mol ^b
	S	M	L	
PhC(Me) ₂ N ₃ (6)		1.0	0.75 (1.9)	173
Ph ₂ C(Me)N ₃ (7)		1.0	1.3	-157
2-PhC ₆ H ₄ C(Me) ₂ N ₃ (8)		1.0	0.69 (2.0)	233
2-PhC ₆ H ₄ C(Ph) ₂ N ₃ (9)		1.0	0.44 (1.1)	493
PhCH ₂ CH ₂ C(CH ₃) ₂ N ₃ (10)		1.0	0.89	70
PhCH(Me)N ₃ (11)	0.70	1.0	0.70	214
<i>t</i> -BuC(Me) ₂ N ₃ (12)		1.0	1.52	-251
(<i>n</i> -Pr) ₂ CHN ₃ (13)	1.0	1.0		0

^a Derived from data presented in the results section. S = small, M = medium, and L = large group. Values in parentheses are thermal migratory aptitudes.⁸ Values have been corrected for statistical preference. ^b Differences in activation energy for the medium and large groups to migrate ($E_a^M - E_a^L = \Delta E_a$).

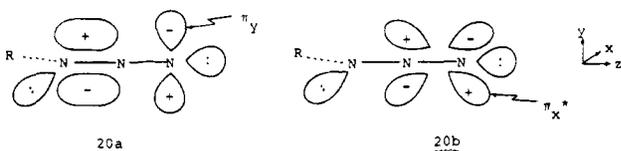
deviate greatly from unity. Where comparisons can be made, the photochemical migratory aptitudes differ considerably from the thermal ones (Table V, parentheses).⁸ This, coupled with the observation that thermally azides **8** and **9** gave rise to **15a** and **15b**,⁸ whereas photochemically they did not, leads us to conclude that the reactive intermediate involved in the photolysis of alkyl azides is different from that involved in the thermolysis.

Before discussing the mechanism of photolysis of alkyl azides in detail, it is apropos to consider some relevant work in this regard. Lewis and Saunders^{10b} found that triplet quenchers have no effect on the direct photolysis of alkyl azides, suggesting that the direct irradiation of alkyl azides proceeds via the singlet manifold. Consistent with this view was the observation that EPR signals of triplet alkylnitrenes could not be observed from the direct irradiation of alkyl azides at

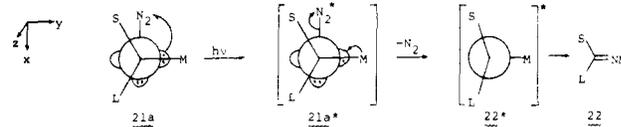
77 K,^{12a} although weak signals were observed at 4 K.^{12b,c} Triplet sensitized photolysis of alkyl azides, however, gave the corresponding alkylnitrenes which were stable for days at 77 K without further irradiation.^{12b,c} Lewis and Saunders¹³ also established that triplet sensitization does lead to decomposition of alkyl azides and estimated the triplet energy of alkyl azides to be in the range of 75–80 kcal/mol. Unfortunately, no product analysis was reported in this study. Summarizing, it can be concluded that: (a) alkyl azides, upon direct irradiation, decompose in the singlet manifold; (b) alkyl azides in the first excited singlet state do not readily undergo intersystem crossing to the triplet azide; (c) triplet alkyl azides are accessible via triplet sensitization; (d) triplet alkyl azides decompose to triplet alkylnitrenes; (e) triplet alkylnitrenes are relatively stable reactive intermediates, persisting for days at 77 K in a solid matrix.

An important question which remains is whether or not direct photolysis of alkyl azides leads to decomposition via intermediate singlet alkylnitrenes. A careful study by Milligan¹⁴ sheds some light on this question. Methyl and methyl-*d*₃ azide were irradiated in dilute argon matrices at 4 K and the course of the reaction was monitored by infrared spectroscopy. No evidence was found for a reactive intermediate, but rather, as the photolysis proceeded, the IR spectrum of the azide disappeared, and the spectrum of methylenimine (or its trideuterated analogue) appeared. It can be concluded either that direct irradiation of methyl azide proceeds from the excited singlet azide to products (methylenimine and nitrogen) in a concerted fashion, or that a “hot” singlet methylnitrene is formed which has sufficient internal energy to rearrange at 4 K. We discuss below the evidence which we feel favors the former process.

Photochemical excitation (ca. 285 nm) of an alkyl azide is thought to involve the promotion of an electron in the highest occupied molecular orbital analogous to the allyl anion HOMO (π_y , **20a**) to a perpendicular antibonding orbital (π_x^* in **20b**).¹⁵



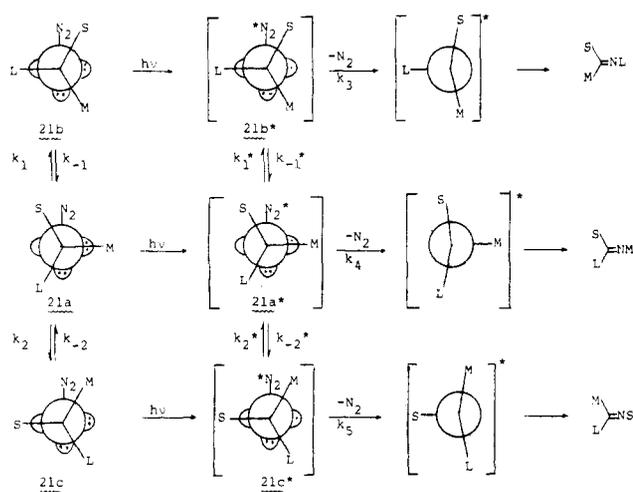
It is generally agreed that the HOMO is π_y as depicted, but there appears to be some disagreement as to the LUMO.¹⁶ Regardless of the nature of the LUMO, an orbital in the *yz* plane becomes electron deficient. If one assumes, for the time being, that migration occurs simultaneously with loss of nitrogen, then the group which migrates would be expected to be that which is aligned with the electron-deficient orbital in the *yz* plane as shown in **21a**.¹⁷ One then has a conformational



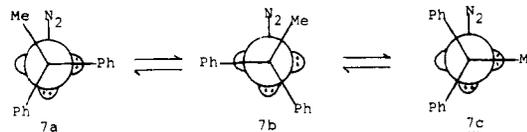
basis for rationalizing migratory aptitudes, as outlined in Scheme II. If one assumes that $k_3, k_4, k_5 \gg k_1^*, k_{-1}^*, k_2^*, k_{-2}^*, k_3^*, k_{-3}^*$ (Scheme II), then the ground state conformational populations would determine the product distributions. On the other hand, if $k_3, k_4, k_5 \ll k_1^*, k_{-1}^*, k_2^*, k_{-2}^*, k_3^*, k_{-3}^*$, then conformational equilibria in the excited states would determine product distributions. We have no sure way of differentiating between the two extreme cases, but it is assumed that the equilibrium distribution in the excited state would not differ drastically from those in the ground state.

Most of the migratory ratios observed by us can now be accounted for by assuming that the most important nonbonded (repulsive) interaction is between the large group (L) and the N₂ moiety of the azido group. Thus on this basis in Scheme II,

Scheme II

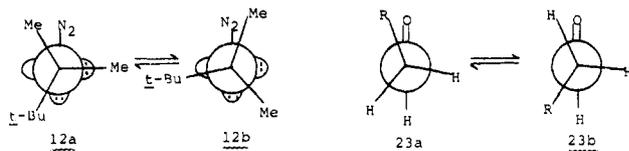


21a would be more stable than **21b** and **21c**, although differentiation between the latter two is difficult (N₂ between L and S but close to S in **21b** and between S and M but close to M in **21c**). Azide **11** is the experimental probe of such a system, where it is found that the medium-sized group (Me) migrates preferentially to the large and small (Ph and H) groups. Where there are two medium-sized groups and one large group, then in Scheme II, where S is replaced by M, **21c** becomes equivalent to **21a** and these are expected to be more stable than **21b**. Azides **6**, **8**, **9**, and **10** are examples in which the medium-sized group migrates preferentially in each case. It is significant that the 2-Ph group has a relatively large effect on the migratory aptitudes of the substituted aryl group (decreasing it relative to a phenyl group), whereas 4-substituents ranging from methoxy to nitro had little effect, if any, in enhancing the migratory aptitude of the substituted phenyl relative to phenyl.^{10a} Thus in this case (azide **9**), the large 2-biphenyl group causes **21a** (\equiv **21c**) (Ph migration) to be significantly more stable than **21b** (2-biphenyl migration). Substituents in the para position, regardless of their electronic nature, could exert no such effect. They would, however, be expected to have an influence should an interaction occur between the α -phenyl group and the azide function (vide infra). It is also important to note that, where the two substituents are Ph and Me, the migration ratio is not constant, but inverts on going from azide **6** to **7**.¹¹ With **7**, the relevant conformations are **7a** (\equiv **7b**) and **7c**, where the former



are predicted to be more stable than the latter, leading to preferential phenyl (large instead of medium group) migration. Thus, our results suggest that there is no “intrinsic” migratory aptitude,^{2h} but rather one which depends on the environment in which the group in question is found. We should also add that recent results from the photolysis of steroidal azides showing very selective migrations^{2f} can be rationalized on the basis of our model, but not on the basis of an earlier theory.¹⁸

Azide **12** appears to be an anomaly, with the large, instead of medium-sized group, migrating preferentially. To account for this, we suggest that the *tert*-butyl group is sufficiently large to experience significant nonbonded repulsion with the sp² orbital in the *yz* plane, making conformer **12b** more stable than **12a**, thereby favoring *t*-Bu migration. Such a reversal in conformational preference has some precedent in the behavior of aldehydes of the type **23** in which **23a** is the preferred conformer for R = Me, Et, *i*-Pr ($\Delta H^\circ = +800, +700, \text{ and } +400$



cal/mol), but with $R = t\text{-Bu}$, **23b** is favored ($\Delta H^\circ = -250$ cal/mol).^{19,20}

The results from the photolysis of azide **13** are bothersome since, on the basis of our model, we might have expected preferential alkyl group migration. We might interpret these results to mean that the energy differences between conformers are too small to observe migratory differences. The smallest conformational energy difference we have observed (70 cal/mol) is that from azide **10** (phenethyl to methyl). The only other secondary azide we have studied is **11**, which had one large group present. It may be that, in the absence of the large group, the cone enclosing the three groups attached to carbon bearing the azido group is narrower (a type of Thorpe-Ingold effect^{22a} in reverse), thereby decreasing the already small interactions with the azido group to the unobservable level. It is also conceivable that, in some cases, e.g., **13** (but not **12**), light absorption leads to an excited state with sufficient excess energy to undergo N-N bond cleavage *before* migration can begin and a free nitrene is formed, as also suggested by Lwowski.^{22b} Clearly, this area requires more investigation.

The implications of the temperature effect on the migratory aptitudes are interesting. The greater selectivity at lower temperature (Tables II-IV) can be rationalized on the basis of Scheme II. Considering the extreme cases, if $k_3, k_4, k_5 \gg k_1^*, k_{-1}^*, \dots$, then observed trends in migratory aptitudes reflect the ground state conformational stabilities. If $k_3, k_4, k_5 \ll k_1^*, k_{-1}^*, \dots$, then the observed ratios reflect excited state conformational stabilities (vide supra). Although rotational isomerism about the alkyl carbon-azido bond has been discussed, and CD and Cotton effects have been used to predict the conformation of an alkyl azide,^{2f} there are a few other experimental data which bear on this problem. Using microwave spectroscopy, methyl azide has been found to have a threefold barrier to internal rotation of 714 cal/mol.²³ This may be compared with the threefold barrier to internal rotation in acetaldehyde, which is 1100 cal/mol.¹⁹ The A value of an azido group is 0.80 kcal/mol and is essentially independent of solvent (from methanol- d_4 to CS₂).²⁴ This may be compared with the A value for an acetyl group which is about 1.2.^{21d,25} (The corresponding A value for an aldehyde group is not listed in two major compilations.^{21d,25}) It might be expected, on the basis of the above discussion, that the aldehyde group is a little "larger" than the azido group. Since rotamer energy differences in substituted acetaldehydes are in the range of 300-1500 cal/mol,¹⁹ one might expect similar, though somewhat lower values for the corresponding azides.

An apparent activation energy difference $\Delta E_a = E_a^M - E_a^L$ for M and L group migration can be calculated from the data in Table V, assuming similar preexponential factors (eq 1),

$$\Delta E_a = E_a^M - E_a^L = RT \ln \frac{k_M}{k_L} \quad (1)$$

where E_a^M and E_a^L are the activation energies for M and L group migrations and k_M and k_L are the first-order rate constants for these processes. The above equation would hold, for example, in Scheme II when S is replaced by M (**21c** \equiv **21a**, $k_4 \equiv k_5$). One can then interpret the ratio k_M/k_L in terms of the following limiting cases: (a) $k_3 = k_4$ and $k_3 \gg k_1^*k_{-1}^*$, k_M/k_L would then reflect the ground state conformational equilibrium, **21a** ($4 \equiv$ **21c**) \rightleftharpoons **21b**; (b) $k_3 = k_4$ and $k_3 \ll k_1^*k_{-1}^*$, k_M/k_L would then reflect the excited state conformational equilibrium, **21a**^{*} (\equiv **21c**^{*}) \rightleftharpoons **21b**^{*}; (c) $k_1 = k_{-1}$ and $k_1^* = k_{-1}^*$, $k_M/k_L = k_3/k_4$, then these ratios would reflect

some "intrinsic" tendency of M and L to migrate. Obviously a much more complex situation could obtain if the above limiting conditions do not hold. We have discussed the above arguments against case c where each group has some "intrinsic" tendency to migrate. The values of E_a shown in Table V might be somewhat low as a reflection of ground state rotamer energy differences (vide supra) and might well reflect case b above instead. It is satisfying to note that, once E_a is calculated from the room temperature photolysis, migratory ratios calculated from eq 1 at other temperatures are in good agreement with experimental values (see last columns in Tables II-IV). This might be indicative that one of the limiting cases holds in these instances at least, rather than a more complex situation, but the latter may obtain with other azides.

Finally, we consider the consequences of a nitrene reactive intermediate. The product-determining step in this scheme must follow the rate-determining loss of nitrogen. It is difficult to conceive of a rationale for the observed migratory ratios and temperature effects. The alkylnitrene is undoubtedly cylindrically symmetrical, and thus no rotational preferences would be expected.

The rationalization presented above accounts for the migratory aptitudes observed by Montgomery and Saunders^{2h} for their structures **1a-f** and **7** (in ref 2h). In addition, the lack of selectivity exhibited by **2-5** is not surprising since two medium-sized groups are similar in size and not much different from the small group.^{25b} Our theory, however, would predict selectivity in one case where none is observed (**6**), and selectivity opposite to that observed in another case (**8**). This might indicate that the aryl ring is playing a role in determining migratory aptitudes, as suggested by Saunders.^{2h} His contention that a $\text{Ph} \cdots \text{N}_\alpha$ interaction manifests itself in the UV spectrum (Fig. 1, ref 2h) is weakened, at least in the general sense, by the fact that both α -methylbenzyl azide (**11**) and **8** (this paper, analogous to **1** in ref 2h) exhibit "normal" UV spectra in cyclohexane solution. It should be noted that we have observed selectivity in one case where the phenyl ring is not attached to the carbon bearing the azido group (**10**) and in another case where no aryl ring is present (**12**). The absence of any effect by para substituents in the phenyl ring has been noted above. We have no explanation at this time for the behavior of 2-cyclohexyl-2-butyl azide and 3-phenyl-3-hexyl azide (**6** and **8** in ref 2h).

In summary, we have presented evidence of nonstatistical migration of groups on an alkyl azide upon direct irradiation, which is best accounted for by a concerted migration-nitrogen loss, without the intervention of an alkylnitrene intermediate.

Experimental Section

General. Melting points are uncorrected. Proton magnetic spectra were obtained on Perkin-Elmer R-12, Varian A-60, or Varian HA-100 instruments, using tetramethylsilane as internal standard. Mass spectra were determined on CEC 21-104, Du Pont 21-491 or CEC 21-100 (high resolution) instruments. Infrared spectra were obtained on a Perkin-Elmer 237B instrument. Ultraviolet spectra were determined on Perkin-Elmer 202 or Cary 14 spectrometers. Gas chromatographic analyses, using internal standards,²⁷ were performed on Varian-Aerograph 1700, 2720 (thermal conductivity), or 2740 (flame ionization) instruments, using one of three columns: column A, 5% SE 30 on Gas Chrom Q (60-80 mesh), packed in copper or stainless steel columns (6 ft \times 0.188 in.); column B, 20% SE 30 (60-80 mesh) on Gas Chrom Q, packed in copper or stainless steel columns (6 ft \times 0.188 in.); column C, 15% H1 EFF 8BP on Gas Chrom Q (60-80 mesh), packed in stainless steel columns (6 ft \times 0.125 in.). A standard carrier gas flow rate of 60 mL/min was used with the thermal conductivity instruments. Peak areas were determined planimetrically or with the aid of a Vidar 6300 digital integrator. Elemental analyses were performed by Atlantic Microlabs.

Commercially available reagents and solvents were usually reagent grade and distilled or recrystallized prior to use. Light petroleum refers

to the fraction 30–60 °C unless otherwise stated. Basic alumina for all column chromatographies was activated at 375 °C for 12 h, followed by cooling in a vacuum desiccator. Molecular sieves [Davison (Fisher Scientific Co.), type 4A, grade 514, 8–12 mesh] were activated at 375 °C for 12 h, cooled, and stored in a vacuum desiccator.

The syntheses of the following compounds, discussed in the text, have been described elsewhere as indicated by the references: azides, **6**,⁸ **7**,^{10a} **8**,⁸ **9**,⁸ **10**,⁸ **13**,²⁸ **14**;⁸ imines, **6A**,⁷ **6B**,⁷ **8A**,⁷ **8B**,⁷ **9A**,⁸ **9B**,⁸ **10A**,⁷ **10B**,⁷ **11C**,²⁹ **14A**;⁸ dihydrophenanthridines, **15a**,⁸ **15b**.⁸ Imines **7A**,^{10a} **7B**,^{10a} **11B**,³⁰ **13A**³¹ previously synthesized by other groups were synthesized in this work by the molecular sieves method.⁷

Photolyses at room temperature or below were carried out in a Vycor apparatus (A) consisting of a clear Dewar container with an insert which, when filled with an appropriate liquid, served to control the temperature at which the photolysis was carried out (ethanol slush, –117 °C; acetone–dry ice, –77 °C). The clearance between the insert which was 50 mm (o.d.), and the inside of the Dewar container was between 2 and 3 mm. Photolyses at elevated temperatures were carried out in a Vycor tube fitted with a condenser apparatus (B). The azide solution (methylcyclohexane) was brought to reflux in an oil bath and then placed in the photolysis apparatus. The heat emitted by the three 100-W medium pressure lamps was sufficient to maintain reflux during the photolysis. All photolyses were carried out in dry, olefin-free, degassed, hydrocarbon solvents.

α -Methylbenzyl Azide (11). α -Methylbenzyl chloride (35.7 g, 250 mmol) was added in one portion to a stirred solution of sodium azide (22 g, 340 mmol) in methylcarbitol (400 mL) and water (70 mL). The mixture was heated to 80 °C for 1 h and allowed to stand at room temperature overnight, and then water (1.5 L) was added. The mixture was extracted with light petroleum (2 \times 600 mL) and the combined extracts were dried (MgSO₄) and concentrated. The residue (37 g) was chromatographed on basic alumina (900 g). Elution with light petroleum (3 L) gave α -methylstyrene (5.8 g, 20%). Elution with light petroleum–benzene (9:1, v/v, 5 L) gave, upon concentration, the azide as a colorless liquid (3.1 g, 8.5%); bp 109–111 °C (37 mm); IR (film) 2100 cm⁻¹; UV (cyclohexane) λ_{\max} 257 (ϵ 195), 283 nm (26); ¹H NMR (CCl₄) δ 7.20 (m, 5-H), 4.44 (q, J = 7 Hz, 1-H), 1.43 (d, J = 7 Hz, 3-H). Anal. (C₈H₉N₃): C, H.

Attempted Preparation of *N*-Ethylideneaniline (11A). Aniline (6.0 g, 64.5 mmol) was added to a mixture of acetaldehyde (31.3 g, 712 mmol) and molecular sieves (20 g) at –77 °C. The mixture was allowed to stand overnight at –77 °C. GLC analysis (column B, 120 °C) showed the presence of aniline (retention time 6.3 min) and a new peak with retention time 8.6 min, in an area ratio of 1:10 respectively. The mixture was filtered at 0 °C and the excess acetaldehyde was removed on a rotary evaporator at –10 °C. As the thick orange-red residue warmed to room temperature an exothermic reaction occurred, raising the temperature to 50–60 °C in 2–3 min. An attempt to distill the resulting material under vacuum (10 μ m) was unsuccessful even with the pot temperature at 185 °C.

2-Azido-2,3,3-trimethylbutane (12). 2-Chloro-2,3,3-trimethylbutane³² (31.0 g, 230 mmol) was added to sodium azide (60 g, 920 mmol) in methyl carbitol (600 mL) and water (150 mL) at 77 °C, and stirred at this temperature for 12 h. Water (2 L) was added and the mixture was extracted with pentane (2 \times 500 mL). The combined pentane extracts were dried (MgSO₄), concentrated, and distilled at atmospheric pressure until the head temperature reached 125 °C. The residue (4.3 g) was chromatographed on basic alumina (400 g) using pentane, to give a colorless liquid (2 g). This was carefully fractionated to give **12** (660 mg, 2%) as a colorless liquid; bp 152–153 °C (760 mm); IR (film) 2100 cm⁻¹; UV (cyclohexane) λ_{\max} 285 nm (ϵ 17); ¹H NMR (CCl₄) δ 1.26 (s, 6-H), 0.93 (s, 9-H). Anal. (C₇H₁₅N₃): C, H.

***N*-Isopropylidene-*tert*-butylamine (12A).** Using the molecular sieves method, **12A** was isolated in 1% yield from acetone and *tert*-butylamine after three careful fractional distillations; bp 38–39 °C (44 mm); IR (film) 1655 cm⁻¹; ¹H NMR (CCl₄) δ 1.85 (s, 6 H), 1.18 (s, 9 H); mass spectrum (70 eV) m/e (rel intensity) 113 (M^+ , 6), 98 (36), 58 (76), 57 (100). Anal. (C₇H₁₅N): C, H.

***N*-(3,3-Dimethyl-2-butylidene)methylamine (12B).** Using the molecular sieves method, **12B** was isolated in 9% yield from pinacolone and methylamine; bp 41–43 °C (45 mm); IR (film) 1660 cm⁻¹; ¹H NMR (CCl₄) 2.98 (q, J = 0.7 Hz, 3-H), 2.70 (q, J = 0.7 Hz, 3-H), 1.04 (s, 9-H); mass spectrum (70 eV) m/e (rel intensity) 113 (M^+ , 3), 98 (5), 57 (6), 56 (100). Anal. (C₇H₁₅N): C, H.

4-Heptylideneimine (13B). Butyronitrile (10.0 g, 145 mmol) in dry

ether (90 mL) was added dropwise to 1.74 M *n*-propyllithium (100 mL, 174 mmol) in ether at –77 °C. The mixture was maintained at –77 °C for 10 h, then stirred at room temperature for 12 h. Absolute methanol (30 mL) was added slowly and the mixture was filtered and concentrated. The residue (7.6 g) was distilled to give the impure imine **13B** (649 mg, 4%) as a colorless liquid; bp 65–73 °C (45 mm). By GLC (column B, 100 °C) this material was shown to contain methanol (2%), butyronitrile (1%), 4-heptanone (3%), and **13B** (94%); IR (film) 3270 (N–H), 1645 cm⁻¹; ¹H NMR (CCl₄) δ 2.12 (t, J = 7 Hz, 4-H), 1.5 (m, 4-H), 0.92 (m, 6-H); mass spectrum (70 eV), m/e 113 (M^+).

Photolysis of Alkyl Azides and Related Experiments. The majority of photolyses were carried out in a standard manner and several representative experiments are reported. The photolysis and workup for azide **9** were atypical and for this reason are described in detail. We also describe the photolysis of **6** and **7** because of differences in observations with another group.¹¹

Photolysis of Azide 8 at –117 °C. The azide (89.7 mg, 0.378 mmol) was dissolved in dry degassed pentane (15 mL) and introduced into apparatus A. Absolute ethanol was introduced into the insert and cooled to a slush using liquid nitrogen. The reaction mixture was then irradiated by three 100-W medium pressure mercury vapor lamps for 0.67 h. Diphenyl ether (26.0 mg, 0.153 mmol) was added as an internal standard to the warmed photolysate. The resulting solution was analyzed directly (no workup) by GLC on column B (190 °C), to give the following yields of products: imine **8A**, 5.2%; imine **8B** (\equiv **8C**), 18.9%; unreacted azide **8**, 74.8%; mass balance, 98.8%. The percentage yields, extrapolated to 100% conversion, are reported in Table II.

A similar experiment in apparatus A at 22 °C gave the following yields: **8A**, 10.5%; **8B**, 30.9%; and **8**, 58.2%; mass balance, 98.7%.

Reaction in apparatus B and boiling methylcyclohexane (101 °C) gave: **8A**, 8.4%; **8B**, 22.2%; **8**, 65.9%; mass balance, 96.5%.

Duplicate runs of the above to different conversions gave similar results, and the averages are reported in Table II.

Irradiation of Imine 8A. The imine (238.5 mg, 1.14 mmol) and diphenyl ether (143.2 mg, 0.843 mmol) were dissolved in dry, degassed cyclohexane (30 mL) and irradiated in apparatus A for 8 h. Aliquots of the reaction mixture were analyzed periodically by GLC, and the results are presented in Table I.

Irradiation of Imine 8B (\equiv **8C).** In an experiment similar to that described for **8A** above, **8B** (\equiv **8C**) (133.6 mg, 0.640 mmol) was still present to the extent of 94% after 4 h of irradiation, as determined by GLC.

Photolysis of Azide 9. The azide (151.1 mg, 0.418 mmol) was dissolved in dry, degassed cyclohexane (50 mL) and irradiated at 25 °C in apparatus A for 24 h, at which time no azide band (2110 cm⁻¹) was observable in the IR spectrum. Diphenyl ether (29.0 g, 0.170 mmol) and triphenylmethane (44.0 mg, 0.182) were added as internal standards and the solution was concentrated to 1 mL by distillation through a 10-cm Vigreux column. Benzene (15 mL), acetic acid (5 mL), and 3 N aqueous hydrochloric acid (5 mL) were added and the mixture was boiled under reflux for 30 h. The aqueous layer was made basic (solid sodium hydroxide), the two layers were separated, and the aqueous layer was extracted with benzene (2 \times 50 mL). The combined benzene extracts were dried (MgSO₄) and concentrated to 5 mL by distillation through a 10-cm Vigreux column. The resulting solution was analyzed on column A: for benzophenone (from imine **9A**), found 70.7%; 2-phenylbenzophenone [(from imine **9B** (\equiv **9C**))], found 14.2%. Corrections from control experiments (see below) led to yields of imines **9A** and **9B** of 76.0 and 16.0%, respectively. A duplicate run gave values of 74.8 and 16.9%.

Irradiation of Imine 9A. The imine (173.6 mg, 0.522 mmol) in dry cyclohexane (50 mL) was irradiated and subjected to workup as described for azide **9**. By GLC, 89.1% of the theoretical amount of benzophenone was accounted for.

Irradiation of Imine 9B (\equiv **9C).** As with imine **9A** above, **9B** (\equiv **9C**) (103.2 mg, 0.310 mmol) in cyclohexane (30 mL), gave 93.0% of the theoretical amount of 2-phenylbenzophenone, as determined by GLC analysis.

Photolysis of Azide 6. The azide (47.6 mg, 0.296 mmol) in dry, degassed cyclohexane (22 mL) was irradiated in apparatus A at 22 °C for 7.5 min. Diphenyl ether (48.1 mg, 0.290 mmol) in cyclohexane (2 mL) was added and the solution was concentrated to 3 mL by distillation through a 10-cm Vigreux column. The resulting solution was analyzed on column C (temperature program, 150–210 °C at 2°/min) to give the following yields: imine **6A**, 4.1%; imine **6B**, 11.7%;

azide **6**, 84.1%; mass balance, 100.3%. Photolyses to higher conversions gave similar product ratios.

Photolysis of Azide 7. The azide (106.6 mg, 0.478 mmol) and nonadecane (34.5 mg, 0.129 mmol) as internal standard were dissolved in dry degassed cyclohexane (2 mL) and irradiated in apparatus A at 22 °C for 0.25 h. GLC analysis on column C (temperature program, 165–200 °C at 2°/min) using the flame ionization detector gave the following yields: imine **7A**, 3.6%; imine **7B** (\equiv **7C**), 1.4%; azide **7**, 94.1%; mass balance 99.0%. Similar runs with conversions from 1 to 40% gave product ratios **7A** to **7B** (\equiv **7C**) in the range of 2.4 to 2.8.

Irradiation of Imines 7A and 7B (\equiv **7C**). Imines **7A** (50.0 mg, 0.256 mmol), **7B** (\equiv **7C**) (49.3 mg, 0.253 mmol), and nonadecane (33.3 mg, 0.124 mmol) were irradiated in apparatus A in pentane (5 mL) at 22 °C for 1.25 h. GLC analysis as described for azide **7** gave the following yields; **7A**, 100%; **7B**, 99.0%.

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- (26) The UV spectra of **6**, **10**, and **11** (in cyclohexane solution, this work) are all very similar and correspond closely with that of **3** in hexane solution given in Figure 1 of ref 2h. We are at a loss to explain why azide **1** in ref 2h [Ph(Me)EtCN₃] and **8** [Ph(Me)₂CN₃] differ so significantly in their UV spectra.
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Kinetics and Mechanism of Nitromethane Chlorination. A New Rate Expression

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Abstract: A kinetic study of the chlorination of nitromethane to trichloronitromethane (chloropicrin) was made. The rate of production of chloropicrin in the pH 6–8 range is first order in both nitromethane and hypochlorite anion. The kinetic dependence on halogenating reagent is a new observation and involves hypochlorite anion acting as a general base. Around pH 12 and above, the mechanism changes to a rate-controlling step of reaction between nitromethane anion or a chlorinated nitromethane anion and hypochlorous acid.

Introduction

The state of halogenation chemistry of nitroalkanes has been briefly summarized by Nielsen.¹ Previous reports have shown that the reaction is both acid and base catalyzed with the im-

portant observation that in acid media the reaction is zero order in halogenating species.^{2a,b} The reaction is subject to general base catalysis^{2a} which has defined the rate-limiting step as proton removal followed by rapid reaction of the nitronate