Migration Aptitudes in the Photolysis of Some Tertiary Alkyl Azides[1]

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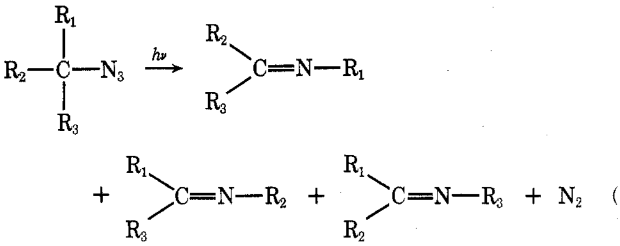
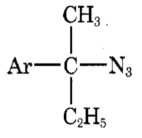
The ethyl/methyl migration aptitudes were determined for photolysis of a series of 2-substituted 2-butyl azides, where the 2 substituent was an aryl group (**1a–f**), $Ph(CH_2)_n$ (**2–4**), or a *n*-propyl group (**5**). Comparison of *n*-propyl/methyl and *n*-propyl/ethyl migration aptitudes were also made (**7–8**). When an aryl group was directly attached to the carbon bearing the azido group, the ethyl/methyl and *n*-propyl/methyl migration aptitudes ran 1.4–1.6, and the ethyl/*n*-propyl migration aptitudes 1.2–1.3. Otherwise, observed migration aptitudes were within experimental error of the statistical values. The results are not in line with ground-state conformational preferences, nor do they show any obvious correlations with expected intrinsic migration aptitudes. The ultraviolet spectrum of **1a** differs significantly from that of an equimolar mixture of toluene and *tert*-amyl azide, suggesting that the aryl group interacts with, and perhaps stabilizes, the excited azide. Anomalous migration aptitudes with bromine-substituted azides appear to result from photolysis of the carbon–bromine bond.

Early work on migration aptitudes in the photolysis of organic azides (eq 1) revealed little or no dependence on the nature of the migrating group. Triarylmethyl azides showed at most a slight preference for the substituted group, regardless of its electronic character, and there appeared to be no significant difference between methyl and phenyl.[3,4] On the basis of these results, reaction via a discrete nitrene was proposed, and supported by trapping experiments in which small amounts of amine corresponding to the nitrene resulted from photolysis in the presence of butyl mercaptan or tributyltin hydride.[4] The possibility that the amine arose from reduction of excited azide could not be ruled out, however.

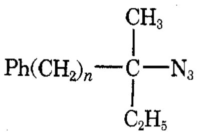

(1)

Migration is not statistical in all cases. Hydrogen migrates up to five times faster than alkyl,[5,6] and cases in which the smaller of two alkyl and/or aryl groups migrate better have been reported.[7,8] These examples of apparent conformational preferences suggest that migration occurs in an excited azide rather than in a nitrene.

The present work on a series of aryl-substituted tertiary alkyl azides was undertaken to determine the effect of the proximity of a phenyl group to the azide function on quantum yields and products of photolysis. The ultraviolet spectra of **1a** and **3** are compared with the spectrum of an equimolar mixture of *tert*-amyl azide and toluene in Figure 1. The spectrum of **3** is rather similar to that of the mixture, but the spectrum of **1a** is markedly different from either. This apparent interaction of the two chromophores is analogous to that reported earlier for phenylacetate esters.[9,10]


$Ar{-}C(CH_3)(C_2H_5){-}N_3$

1a, Ar = C_6H_5
b, Ar = p-BrC_6H_4
c, Ar = p-ClC_6H_4
d, Ar = m-ClC_6H_4
e, Ar = m-BrC_6H_4
f, Ar = 3,4-$Cl_2C_6H_3$


$Ph(CH_2)_n{-}C(CH_3)(C_2H_5){-}N_3$

2, $n = 1$
3, $n = 2$
4, $n = 3$

In the absence of interactions between the chromophores, one would expect absorption of light by the benzene ring and energy transfer from the benzene ring to the azide prior to loss of nitrogen and rearrangement, since substituted benzenes absorb at least ten times more strongly than alkyl azides in the 253.7-nm region. The quantum yields for nitrogen evolution (Table I) do not, however, show any consistent trend from **1a** to **4**. Some caution is needed in interpreting these figures, for it was not always possible to remove olefin and alcohol impurities completely from the azide samples. The minimum purity was 94%, so neither is major error expected from this source.

The azides used for quantum yields and migration aptitudes were prepared by standard procedures (see Experimental Section). Photolyses were carried out on carefully degassed solutions, except as otherwise noted, to low (<8%) conversions to minimize secondary reactions. The products were hydrolyzed to mixtures of the corresponding ketones, which were analyzed as such by GLC or reduced to the corresponding alcohols and then analyzed. Control experiments showed that hydrolysis and reduction were complete, and that there was no interference from unreacted azide or its decomposition products. Known mixtures of azides and ketones were run through the complete workup procedure to calibrate the analyses. The migration aptitudes reported in Tables II and III were reproducible to 10% or better.

Examination of Table II reveals an interesting dichotomy. The results for **1a–f** show a clear preference for ethyl over methyl migration (usually 1.4–1.6), while the results for **2–4**

Table I. Quantum Yields of Nitrogen Evolution for the Photolysis of 2-Substituted 2-Butyl Azides[a]

Compd	Φ_{N_2} for photolysis time[c] 6 min	18 min	60 min
1a	0.32 ± 0.01	0.30 ± 0.01	0.19 ± 0.01
2	0.16[b]	0.27 ± 0.10	0.14[b]
3	0.57[b]	0.53 ± 0.02	0.42[b]
4	0.45 ± 0.02	0.37 ± 0.01	0.22 ± 0.01

[a] Run in a Rayonet RPR-208 reactor with RUL 2537 (253.7 nm) lamps in hexane solution. A uranyl oxalate actinometer was used, and Φ corrected for light not absorbed by the azide. [b] Single run only. [c] Percent of theoretical yield of nitrogen was below 10% in most cases, but 10–15% in a few.

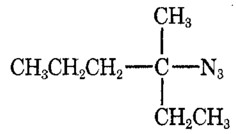
Table II. Ethyl/Methyl Migration Aptitudes in the Photolysis of 2-Substituted 2-Butyl Azides[a]

Entry no.	Compd	λ, nm	Solvent	Et/Me
1	**1a**	253.7	Hexane	1.41 ± 0.04
2	**1b**	253.7	Hexane	1.43 ± 0.07
3	**1b**	253.7	Hexane	1.99 ± 0.05[b]
4	**1c**	253.7	Hexane	1.38 ± 0.01
5	**1d**	253.7	Hexane	1.36 ± 0.02
6	**1e**	253.7	Hexane	1.31 ± 0.05
7	**1e**	253.7	Hexane	1.97 ± 0.08[b]
8	**1f**	253.7	Hexane	1.27 ± 0.01
9	**1a**	300	Hexane	1.56 ± 0.03
10	**1b**	300	Hexane	1.31 ± 0.04
11	**1e**	300	Hexane	1.38 ± 0.01
12	**1f**	300	Hexane	1.37 ± 0.02
13	**2**	253.7	Hexane	1.10 ± 0.20
14	**3**	253.7	Hexane	1.01 ± 0.04
15	**4**	253.7	Hexane	1.03 ± 0.03
16	**2**	300	Hexane	1.07 ± 0.01
17	**3**	300	Hexane	1.08 ± 0.05
18	**4**	300	Hexane	1.03 ± 0.03
19	**1a**	300	Chloroform	1.46 ± 0.04[b]
20	**1a**	300	Benzene	1.60 ± 0.03[b]
21	**1a**	300	Mesitylene	1.50 ± 0.03[b]
22	**3**	300	Chloroform	1.06 ± 0.02[b]
23	**3**	300	Benzene	1.16 ± 0.03[b]
24	**3**	300	Mesitylene	1.07 ± 0.01[b]
25	**1b**	253.7	Hexane	1.53 ± 0.03[c]
26	**1e**	253.7	Hexane	1.59 ± 0.03[c]

[a] Run in a Rayonet RPR-208 reactor with RUL 2537 (253.7 nm) or RUL 3000 (300 nm) lamp with Pyrex filter. Reactions were carried to less than 8% and in 0.05–0.08 M degassed solution unless otherwise noted. Each number is the average of three or more runs. [b] Not degassed. [c] In presence of 0.7 M 2,3-dimethyl-2-butene.

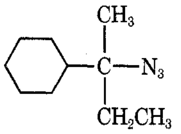
are essentially within experimental error of showing no ethyl:methyl preference. No significant effect of wavelength, solvent, or para substituent is discernible. The only entries out of line are 3 and 7, for undegassed photolyses of **1b** and **1e**, and these will be commented on later.

Table III gives further information on these trends. It is evidently not just the bulk of the aryl group which is responsible for the Et/Me preference in **1a–f**, for the cyclohexyl group in **6** produces no such preference. Similarly, no differences in the tendencies of methyl, ethyl and *n*-propyl to migrate in **5** are distinguishable. There is, however, an *n*-Pr/Me preference of 1.4–1.5 in **7**, and, surprisingly, an Et/*n*-Pr preference of 1.2–1.3 in **8**. The results as a whole exclude any conformational effect depending simply on the bulk of the groups attached to the α carbon.

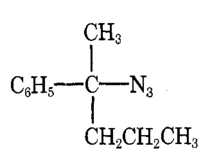


$CH_3CH_2CH_2—\overset{CH_3}{\underset{CH_2CH_3}{C}}—N_3$

5

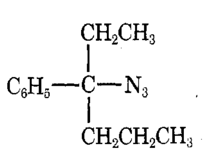


6



$C_6H_5—\overset{CH_3}{\underset{CH_2CH_2CH_3}{C}}—N_3$

7



$C_6H_5—\overset{CH_2CH_3}{\underset{CH_2CH_2CH_3}{C}}—N_3$

8

The absence of any regular dependence on steric requirements in turn casts doubt on the assertion that migration tendencies are determined mainly or entirely by ground-state conformational effects.[5,8] The order Me < Et > *n*-Pr suggests that at least two effects are operating. Ground-state conformational preferences may well be decisive with the very hindered 2-biphenylyl compounds studied by Abramovitch and Kyba,[7,8] but it seems that some role must be ascribed to intrinsic migration aptitudes in other cases. If the rates of migration and of rotation about the carbon–nitrogen bond of the

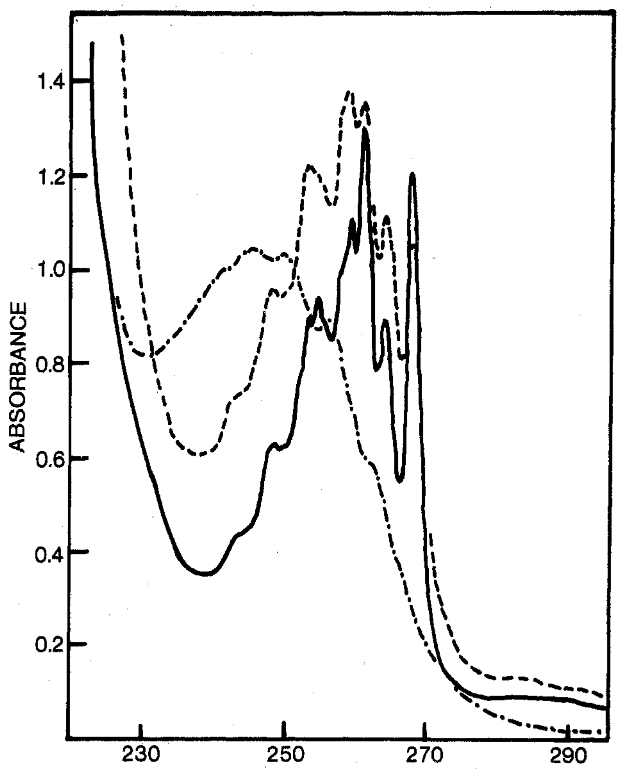


Figure 1. Ultraviolet spectra in hexane solution of 2-phenyl-2-butyl azide (**1a**), 0.00145 M, - · - ·; 3-methyl-1-phenyl-3-pentyl azide (**3**), 0.0029 M, - - -; and an equimolar mixture of *tert*-amyl azide and toluene, 0.0029 M, —.

Table III. Miscellaneous Migration Aptitudes in the Photolysis of 2-Substituted 2-Butyl Azides[a]

Entry no.	Compd	λ, nm	Migrating groups, R′:R	R′/R
1	**5**	300	Et:Me	0.99 ± 0.02
2	**5**	300	*n*-Pr:Me	1.05 ± 0.03
3	**5**	300	Et:*n*-Pr	0.94 ± 0.04
4	**6**	300	Et:Me	1.00 ± 0.03
5	**1a**	300	Et:Me	1.56 ± 0.06
6	**1a**	253.7	Et:Me	1.48 ± 0.03
7	**1a**	253.7	Ph:Me	1.04 ± 0.06
8	**7**	300	*n*-Pr:Me	1.41 ± 0.05
9	**7**	253.7	*n*-Pr:Me	1.52 ± 0.07
10	**7**	253.7	Ph:Me	0.93 ± 0.03
11	**8**	300	Et:*n*-Pr	1.31 ± 0.02
12	**8**	253.7	Et:*n*-Pr	1.21 ± 0.04

[a] Conditions same as in footnote *a* of Table II, except that nondegassed solutions were used.

excited azide are comparable, then intrinsic migration aptitudes may affect the results unless there are fairly large energy differences between the possible conformations.

There may also be some specific effect of aryl substitution on the α-carbon atom. With one marginal exception (2-phenylethyl:methyl of 0.89:1.00[8]), the only cases of nonstatistical migration in tertiary alkyl azides involve reactants possessing α-aryl groups. The α-aryl group might interact with the orbitals on the nitrogen attached to carbon so as to stabilize and increase the discrimination of the electrophilic nitrogen resulting from a π,π* excitation,[11] or so as to favor one conformation of the excited azide over another. The fact that the uv spectrum of **1a** differs markedly from that of **3** and that of an equimolar mixture of *tert*-amyl azide and toluene (Figure 1) provides evidence for interaction of the α-aryl and azide functions in the singlet excited state. The interaction cannot be very strong or specific, however, for substituents in the aryl group have little or no effect on ethyl:methyl migration aptitudes (Table II), and phenyl:methyl migration aptitudes are near unity (Table III). A more detailed analysis of the complex pattern of small migrational preferences (and the frequent lack thereof) in the photolysis of tertiary alkyl azides does not seem worthwhile at the present time.

We now return to the results with **1b** and **1e** in nondegassed solution (entries 3 and 7, Table II). These bromo compounds were originally studied to see if a heavy-atom substituent would affect the results by promoting intersystem crossing.[12] The unusual migration aptitudes were, however, found only in undegassed solution. The values in degassed solution (entries 2 and 6, Table II) were not out of line with the values from other compounds in the **1a–f** series. Similarly, "normal" migration aptitudes are observed in the presence of 2,3-dimethyl-2-butene (entries 25–26, Table II) and several other olefins, but the quantum yields for nitrogen evolution from **1b** and **1e** remain 0.20 ± 0.02 in either the presence or absence of *cis*-4-methyl-2-pentene.

This last fact indicates that bromine substitution does not interfere with loss of nitrogen. Table IV shows that **1b** and **1e** cause cis–trans isomerization when photolyzed in the presence of *cis*-4-methyl-2-pentene, as does 4-bromotoluene. That the bromine is responsible for the isomerization is shown by the fact that isomerization is ca. 10^4 less efficient with azides lacking a bromo substituent. Finally, some unsubstituted azide (**1a**) is isolated after partial photolysis of **1b** and **1e**.

The most likely explanation of these results is that photolysis of **1b** and **1e** generates bromine atoms, which can then cause cis–trans isomerization of added olefin via reversible addition.[13] In the absence of olefin, the bromine atoms can cause selective destruction of product imines. That the migration aptitudes are out of line only in undegassed solution is puzzling, but may indicate that oxygen is trapping an otherwise reversibly formed addition product from the imine and a bromine atom. The quantum yields in Table IV suggest that as much as 30% of the azide may be losing bromine atoms, but quantitative estimates are uncertain. Determination of the proportion of debrominated azide in the products is precluded by partial thermal decomposition in the GLC injector of both substituted and unsubstituted azide, and some of the bromine atoms could be generated from product imine rather than starting azide, which would cloud the significance of any analysis for debrominated products.

Table IV. Quantum Yields for Isomerization of *cis*-4-Methyl-2-pentene[a]

Sensitizer	$\Phi_{c \to t}{}^{c}$
3	8×10^{-4}
1a	8×10^{-4}
1c	8×10^{-4}
1f	8×10^{-4}
1e	1.2×10^{0}
1b	1.2×10^{0}
4-Bromotoluene	4×10^{0}

[a] Conditions the same as in footnote *a* of Table I, except that degassed heptane solutions were used. [b] Not corrected for back reaction.

Experimental Section[14]

2-Cyclohexyl-2-butanol. Cyclohexylmagnesium bromide and 2-butanone gave 2-cyclohexyl-2-butanol in 68% yield, bp 57–57.5 °C (0.45 mm), n^{25}D 1.4702. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.91. Found: C, 76.83; H, 12.96.

2-Phenyl-2-butanol was obtained from phenylmagnesium bromide and 2-butanone in 75% yield, bp 47.5 °C (0.08 mm), n^{20}D 1.5199 [lit.[15] bp 97 °C (15 mm), n^{20}D 1.5195].

2-Aryl-2-butanols, except for 2-phenyl-2-butanol, were prepared from ethylmagnesium bromide and the appropriate acetophenone.

2-(3-Bromophenyl)-2-butanol was obtained in 77% yield, bp 73 °C (0.1 mm), n^{24}D 1.5537. Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72; Br, 34.88. Found: C, 52.43; H, 5.80; Br, 34.92.

2-(4-Bromophenyl)-2-butanol was obtained in 72% yield, bp 76–78 °C (0.04 mm), n^{25}D 1.5530. Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72; Br 34.88. Found: C, 52.32; H, 5.66; Br, 35.08.

2-(3-Chlorophenyl)-2-butanol was obtained in 66% yield, bp 135–138 °C (28 mm), $n^{36.5}$D 1.5300. Anal. Calcd for $C_{10}H_{13}ClO$: C, 65.04; H, 7.10; Cl, 19.20. Found: C, 65.05; H, 6.92; Cl, 19.28.

2-(3,4-Dichlorophenyl)-2-butanol was obtained in 73% yield, bp 102–103 °C (4.2 mm), n^{20}D 1.5525. Anal. Calcd for $C_{10}H_{12}Cl_2O$: C, 54.81; H, 5.52; Cl, 32.36. Found: C, 54.84; H, 5.46; Cl, 32.25.

3-Methyl-3-hexanol was obtained in 94% yield from ethylmagnesium bromide and 2-pentanone, bp 139.5–141 °C (757 mm) (lit.[16] bp 143 °C).

3-Methyl-6-phenyl-3-hexanol was obtained in 78% yield from 3-phenylpropylmagnesium bromide and 2-butanone, bp 80–82 °C (0.35 mm), n^{20}D 1.5053 [lit.[17] bp 154–163 °C (23 mm), n^{25}D 1.5050].

3-Methyl-1-phenyl-3-pentanol was obtained in 73% yield from 2-phenylethylmagnesium bromide and 2-butanone, bp 70–72 °C (0.1 mm), n^{27}D 1.5083 [lit.[18] bp 132–133 °C (12 mm), n^{20}D 1.5114].

3-Phenyl-3-hexanol was obtained from ethylmagnesium bromide and butyrophenone, bp 105–110 °C (3 mm) [lit[19] bp 134 °C (27 mm)].

2-Phenyl-2-pentanol was obtained from phenylmagnesium bromide and 2-pentanone, bp 115–118 °C (13 mm) [lit.[20] bp 100–102 °C (5 mm)].

Preparation of Azides. The azides were prepared from the corresponding tertiary alcohols by a procedure similar to that used by Saunders and Caress[21–23] for 2-phenyl-2-propyl azide. The azides were all obtained as oils which could not be crystallized and which decomposed on attempted distillation at 0.5 mm. Chromatography on alumina effected decolorization, but failed to remove all olefin and/or unreacted alcohol. Shaking a solution of the azide in hexane with alumina was as effective as chromatography, leaving less than 5–6% of impurities as judged by ir and NMR spectra, GLC analysis, and the amount of nitrogen evolved on thermolysis. The azides were stable in the dark at 0 °C for at least several months. Two typical preparations are described below.

3-Phenyl-3-hexyl Azide. To a solution of 0.2 mol of hydrazoic acid in chloroform[24] and 0.1 mol of 3-phenyl-3-hexanol was added dropwise with stirring over 1 h 0.1 mol of concentrated sulfuric acid. The mixture was stirred for another 1 h and neutralized with 20% sodium hydroxide, and the chloroform layer separated. The chloroform solution was washed twice with 10% sodium bicarbonate and five times with water, and dried over anhydrous magnesium sulfate. Removal of the chloroform in vacuo left a pale yellow liquid which was decolorized by shaking a hexane solution with alumina. Removal of the hexane left a colorless liquid with no ir absorption at 3600 cm^{-1} (hydroxyl) and a strong band near 2100 cm^{-1} (azide).

2-(4-Chlorophenyl)-2-butyl and 2-(4-methoxyphenyl)-2-butyl azides were prepared in 50–60% yields from mixtures of the corresponding alcohols and their olefinic dehydration products by reaction with hydrazoic and trichloroacetic acids.[25]

1-Cyclohexylethanol was prepared in 62% yield from cyclohexylmagnesium bromide and acetaldehyde, bp 58–61 °C (3 mm) [lit.[26] 85–87 °C (17 mm)].

Cyclohexyl methyl ketone was obtained in 92% yield from 1-cyclohexylethanol by chromic acid oxidation according to the procedure of Van Woerden.[27] The product had bp 62–63 °C (7 mm), $n^{32}D$ 1.4478, 2,4-dinitrophenylhydrazone mp 140–141 °C [lit.[28] bp 60–61 °C (8 mm), $n^{27}D$ 1.4500, 2,4-dinitrophenylhydrazone[29] mp 149–151 °C].

1-Cyclohexylpropanol was prepared in 70% yield from cyclohexylmagnesium bromide and propionaldehyde, bp 91–92 °C (15 mm), $n^{40}D$ 1.4585 [lit.[30] bp 96 °C (18 mm), $n^{20}D$ 1.4688].

Cyclohexyl ethyl ketone was obtained in 91% yield by chromic acid oxidation of 1-cyclohexylpropanol.[31] The product had bp 62 °C (4 mm), 2,4-dinitrophenylhydrazone mp 150.5–152 °C [lit.[32] bp 73–77 °C (8 mm), 2,4-dinitrophenylhydrazone mp 150–151 °C].

6-Phenyl-3-hexanol was prepared in 87% yield from 3-phenylpropylmagnesium bromide and propionaldehyde, bp 81–82 °C (0.25 mm) [lit.[33] bp 145–146 °C (14 mm)].

6-Phenyl-3-hexanone was obtained in 93% yield by chromic acid oxidation[31] of 6-phenyl-3-hexanol. The product had bp 67 °C (0.25 mm), $n^{25}D$ 1.5314, semicarbazone mp 150–151 °C [lit.[33] bp 132–134 °C (14 mm), $n^{19}D$ 1.515, semicarbazone mp 153–154 °C].

1-Phenyl-3-pentanol was prepared in 63% yield from 2-phenylethylmagnesium bromide and propionaldehyde, bp 91–95 °C (1.2 mm) (lit.[34] bp 130 °C (15 mm)].

1-Phenyl-3-pentanone was obtained in 56% yield by chromic acid oxidation[31] of 1-phenyl-3-pentanol. The product had bp 62 °C (0.3 mm), $n^{29}D$ 1.5045 [lit.[35] bp 130–132 °C (19 mm)].

5-Phenyl-2-pentanone. To 200 ml of dry ethanol in a flask fitted with a reflux condenser and a dropping funnel was added 7.6 g (0.33 g-atom) of sodium. After the sodium had dissolved, 43 g (0.33 mol) of ethyl acetoacetate was added dropwise over 1 h. The mixture was refluxed for 1 h and 65 g (0.35 mol) of 2-phenylethyl bromide added slowly. The mixture was then refluxed for 21 h, cooled, filtered, and distilled to yield 71% of the alkylation product. Fifty grams (0.21 mol) of this product was heated at 90 °C for 5 h with 330 ml of 5% sodium hydroxide. The mixture was treated with 150 ml of 50% (by weight) sulfuric acid, stirred for 5 h at 90 °C, cooled to room temperature, and stirred for another 48 h. The acid solution was extracted with ether, and the extracts dried over sodium sulfate and distilled to give 87% of 5-phenyl-2-pentanone, bp 132–134 °C (17 mm), $n^{25}D$ 1.5068 [lit. bp 134 °C (17 mm),[36] $n^{25}D$ 1.5070[37]].

1-(3-Chlorophenyl)propanol was obtained in 85% yield from ethylmagnesium bromide and 3-chlorobenzaldehyde, bp 75–76 °C (0.4 mm), $n^{25}D$ 1.5357. Anal. Calcd for $C_9H_{11}ClO$: C, 63.35; H, 6.50; Cl, 20.77. Found: C, 63.39; H, 6.45; Cl, 20.85.

3′-Chloropropiophenone resulted in 93% yield from the chromic acid oxidation[31] of 1-(3-chlorophenyl)propanol, mp 46–47 °C (lit.[38,39] mp 45–46 °C).

1-(3-Bromophenyl)propanol was obtained in 77% yield from ethylmagnesium bromide and 3-bromobenzaldehyde, bp 115 °C (2.7 mm) [lit.[40] bp 125–130 °C (11 mm)].

3′-Bromopropiophenone resulted in 90% yield from the chromic acid oxidation[31] of 1-(3-bromophenyl)propanol, mp 40–41 °C (lit.[38,39] 37.5–40 °C).

1-(3,4-Dichlorophenyl)propanol was obtained in 82% yield from ethylmagnesium bromide and 3,4-dichlorobenzaldehyde, bp 78–79 °C (0.04 mm), $n^{22}D$ 1.5550. Anal. Calcd for $C_9H_{10}Cl_2O$: C, 52.71; H, 4.92; Cl, 34.57. Found: C, 52.65; H, 4.92; Cl, 34.70.

3′,4′-Dichloropropiophenone resulted in 64% yield from the chromic acid oxidation[31] of 1-(3,4-dichlorophenyl)propanol, mp 42–43 °C, oxime mp 116–117 °C (lit.[41] mp 44 °C, oxime mp 121–122 °C).

Acetophenone Ethylimine. A solution of 0.50 mol of benzonitrile was added dropwise with stirring to 0.49 mol (163 ml) of 3 M methylmagnesium bromide in ether. The mixture was refluxed for 18 h and cooled, and 200 ml of 9 M ethylamine in anhydrous methanol added over 2 h. After 2 h at reflux, the mixture was treated successively with 17.5 ml of water and 21 ml of 20% sodium carbonate, and then cooled. The suspension was extracted with ether, and the extracts dried over sodium sulfate and then fractionated to yield 35% of product, bp 52–55 °C (0.5 mm), $n^{24}D$ 1.5367 [lit.[43] bp 44 °C (0.13 mm), $n^{20}D$ 1.5362]. Analysis by GLC indicated ca. 3% contamination with acetophenone.

Acetophenone phenylimine was obtained in 96% yield by the procedure of Saunders and Caress,[21] mp 38.5–40 °C (lit.[44] 41 °C).

Benzophenone phenylimine was obtained by adding 0.39 mol of distilled aniline to 0.10 mol of dichlorodiphenylmethane over a 1-h period. The resulting mixture was filtered and the product recrystallized from ethanol, mp 112–113 °C (lit.[45] 114 °C).

Benzophenone ethylimine was prepared in the same manner as benzophenone phenylimine from dichlorodiphenylmethane and ethylamine. The product had bp 137–138 °C (3.5 mm) [lit.[46] 144 °C (7 mm)]. Analysis by GLC showed ca. 1% benzophenone.

2-Butanone Phenylimine. 2-Butanone diethyl ketal was obtained from 0.50 mol of 2-butanone, 0.50 mol of ethyl orthoformate, and 0.09 mol of ammonium chloride in 60 ml of absolute ethanol. The mixture was allowed to stand for 7 days and then distilled to yield 62% of ketal, bp 44–45 °C (25 mm) [lit.[47] 41 °C (16 mm)]. A mixture of 0.1 mol of the ketal and 0.1 mol of aniline was heated until ethanol no longer distilled. Vacuum distillation of the residue gave 92% of 2-butanone phenylimine, bp 53 °C (2.0 mm) [lit.[48] 106–108 °C (25 mm)].

Propiophenone Phenylimine. Propiophenone diethyl ketal was prepared in the same manner as 2-butanone diethyl ketal, bp 66 °C (0.8 mm) [lit.[49] 93–96 °C (6 mm)]. The ketal was then heated with distilled aniline until ethanol no longer distilled to yield a solid which was recrystallized from ethanol, mp 51–53 °C (lit.[50] 50 °C).

Propiophenone Methylimine. The same procedure as for acetophenone ethylimine[42] was used, preparation of the Grignard complex from ethylmagnesium bromide and benzonitrile, followed by treatment with ethanolic methylamine. Distillation afforded the imine, bp 94 °C (16 mm), $n^{28.5}D$ 1.5270 [lit.[42] bp 102 °C (20 mm), $n^{20}D$ 1.5299]. The imine was very sensitive to atmospheric moisture. Freshly prepared material contained ca. 20% of propiophenone as shown by ir and GLC, and further hydrolysis occurred when it was kept for more than a few days at 0 °C.

Photolysis Procedure. Solvents were Mallinckrodt Spectrograde. Solutions 0.05–0.08 M in azide were used, and the percent conversion kept below 8% to minimize secondary reactions. Degassing was conducted using six freeze–pump–thaw cycles on a vacuum line which could be evacuated to less than 10^{-5} Torr. A Rayonet reactor, Model RPR-208, was used with a merry-go-round apparatus. Photolyses were conducted at 253.7 nm in quartz tubes with unfiltered light from RUL 2537 lamps, and photolyses at 300 nm with light from RUL 3000 lamps and Kimax tubes and/or Pyrex filters. Uranyl oxalate actinometry was used, assuming quantum yields of oxalate decomposition of 0.60 at 253.7 nm and 0.57 at 300 nm.[51,52] Correction for light absorbed by the actinometer but not the azides (>300 nm) was made by dividing the observed quantum yield by 0.74 (obtained by irradiating the actinometer with light from RUL 2537 lamps through a Pyrex filter). Azide concentrations for quantum yield determinations were chosen such that >99.9% of the incident 253.7-nm light was absorbed by the solution. Nitrogen yields were determined by carrying out the photolyses in degassed tubes equipped with break seals. The tubes were then slowly frozen in liquid nitrogen from the bottom up. The break seal was opened to the evacuated system and the nitrogen pumped into a gas buret with a Toepler pump. The stopcock to the photolysis tube was closed and the contents thawed with warm water. The freezing and pumping process was repeated three times. The nitrogen yield was calculated from the pressure, temperature, and volume of the sample assuming the ideal gas law.

Determination of Photolysis Products. The photolyzed sample, including solvent, was added to 5 ml of 10% sulfuric acid and the mixture stirred magnetically and heated to 80–90 °C under a reflux condenser for 1 h. The mixture was cooled and neutralized with saturated sodium bicarbonate. The organic layer was separated and the aqueous layer extracted with two 2-ml portions of chloroform. In most instances the combined organic layer and extracts were reduced by stirring with excess sodium borohydride in 95% methanol for 1 h, so as to avoid overlap in the GLC analysis of the thermal decomposition peaks of the azide and the ketone peaks of the hydrolysis products. Excess borohydride was removed by filtration and the resulting solution analyzed.

Analyses were done on a Hewlett-Packard F and M Model 700 gas chromatograph equipped with a flame ionization detector and a Model 240 temperature programmer. The ethyl/methyl migration aptitudes were the 1-aryl-1-propanol/1-arylethanol ratios determined on a 6 ft × 0.125 in. column of 20% FFAP (Applied Science) on Anakrom ABS 100/110 (Analabs) at oven temperatures of 135–190 °C, injector temperatures of 210–280 °C, and nitrogen flow rates of 24–91 ml/min. Retention times ranged from 8 to 37 min. Cyclohexanol or cyclopentanol were used as internal standards to permit comparison with the aryl migration product, 2-butanol, which was analyzed on a 10 ft × 0.125 in. column of Emulphor-O (Applied Science) on Chromosorb P (Varian) employing programmed runs (10 °C/min) from 85 to 152 °C. The products from 3-azido-3-methylhexane were analyzed on a 10.5 ft × 0.125 in. column of Chromosorb 101 (no liquid phase) at 150 °C and 61 ml/min.

Control Experiments. Authentic samples of the ketone and alcohol products were coinjected with the product mixtures. Detector response was calibrated with known mixtures of azide and ketones run through the entire hydrolysis and reduction procedure. No acid-catalyzed decomposition products resulted when the azides alone were put through the hydrolysis and reduction procedures. Azides used for photolysis runs were shown to be free of ketone by GLC. Acetophenone ethylimine and propiophenone methylimine were >99.9% hydrolyzed in 1 h. Reduction of known ketones by the standard procedure gave >99.9% reduction.

Registry No.—**1a,** 58977-18-7; **1b,** 58977-19-8; **1c,** 58977-20-1; **1d,** 58977-21-2; **1e,** 58977-22-3; **1f,** 58977-23-4; **2,** 58977-24-5; **3,** 58977-25-6; **4,** 58977-26-7; **5,** 58977-27-8; **6,** 58977-28-9; **7,** 58977-29-0; **8,** 58977-30-3; 2-cyclohexyl-2-butanol, 58977-31-4; 2-phenyl-2-butanol, 1565-75-9; 2-(3-bromophenyl)-2-butanol, 58977-32-5; 2-(4-bromophenyl)-2-butanol, 58977-33-6; 2-(3-chlorophenyl)-2-butanol, 58977-34-7; 2-(3,4-dichlorophenyl)-2-butanol, 58977-35-8; 3-methyl-3-hexanol, 597-96-6; 3-methyl-6-phenyl-3-hexanol, 5406-61-1; 3-methyl-1-phenyl-3-pentanol, 10415-87-9; 3-phenyl-3-hexanol, 20731-93-5; 2-phenyl-2-pentanol, 4383-18-0; hydrazoic acid, 14343-69-2; 2-(4-chlorophenyl)-2-butanol, 3947-53-3; cyclohexyl methyl ketone, 823-76-7; 1-phenyl-2-methyl-2-butanol, 772-46-3; cyclohexyl ethyl ketone, 4361-28-8; 6-phenyl-3-hexanone, 58977-36-9; 1-phenyl-3-pentanone, 20795-51-1; 5-phenyl-2-pentanone, 2235-83-8; 3-chloropropiophenone, 34841-35-5; 3-bromopropiophenone, 19829-31-3; 3′,4′-dichloropropiophenone, 6582-42-9; acetophenone ethylimine, 6907-72-8; acetophenone phenylimine, 1749-19-5; benzophenone phenylimine, 574-45-8; benzophenone ethylimine, 27126-11-0; 2-butanone phenylimine, 40296-03-5; propiophenone phenylimine, 14752-72-8; propiophenone methylimine, 29640-04-8; *cis*-4-methyl-2-pentene, 691-38-3.

References and Notes

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(2) NDEA Fellow.
(3) W. H. Saunders, Jr., and E. A. Caress, *J. Am. Chem. Soc.*, **86**, 861 (1964).
(4) F. D. Lewis and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **90**, 7031 (1968).
(5) R. M. Moriarty and M. Rahman, *Tetrahedron*, **21**, 2877 (1965).
(6) R. M. Moriarty and R. C. Reardon, *Tetrahedron*, **26**, 1379 (1970).
(7) R. A. Abramovitch and E. P. Kyba, *Chem. Commun.*, 265 (1969).
(8) R. A. Abramovitch and E. P. Kyba, *J. Am. Chem. Soc.*, **93**, 1537 (1971).
(9) R. Brainard and H. Morrison, *J. Am. Chem. Soc.*, **93**, 2685 (1971).
(10) M. L. Yarchak, J. C. Dalton, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **95**, 5228 (1973).
(11) W. D. Closson and H. B. Gray, *J. Am. Chem. Soc.*, **85**, 290 (1963).
(12) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, Chapter 7.
(13) C. Walling, "Free Radicals in Solution", Wiley, New York, N.Y., 1957, p 302.
(14) Melting points are corrected; boiling points are uncorrected. Analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.
(15) K. Serijan and P. Wise, *J. Am. Chem. Soc.*, **74**, 365 (1952).
(16) P. Ginningo and M. Hauser, *J. Am. Chem. Soc.*, **60**, 2581 (1938).
(17) H. Adkins and J. Davis, *J. Am. Chem. Soc.*, **71**, 2955 (1949).
(18) H. Pines and J. Arrigo, *J. Am. Chem. Soc.*, **79**, 4958 (1957).
(19) H. Gilman and R. Meals, *J. Org. Chem.*, **8**, 126 (1943).
(20) M. Protiva, O. Exner, M. Borovicka, and J. Pliml, *Chem. Listy*, **46**, 37 (1952).
(21) W. H. Saunders, Jr., and E. A. Caress, *J. Am. Chem. Soc.*, **86**, 861 (1964).
(22) A. L. Logothetis, *J. Am. Chem. Soc.*, **87**, 749 (1965).
(23) C. L. Arcus and R. J. Mesley, *J. Chem. Soc.*, 178 (1953).
(24) H. Wolff, *Org. React.*, **3**, 327 (1946).
(25) C. H. Gudmundsen and W. E. McEwen, *J. Am. Chem. Soc.*, **79**, 329 (1957).
(26) W. K. Johnson, *J. Org. Chem.*, **24**, 864 (1959).
(27) S. Van Woerden, *Recl. Trav. Chim. Pays-Bas*, **45**, 124 (1926).
(28) S. L. Friess and N. Farnham, *J. Am. Chem. Soc.*, **72**, 5518 (1950).
(29) J. Meinwald and S. L. Emerman, *J. Am. Chem. Soc.*, **78**, 5087 (1956).
(30) D. Nightingale and H. D. Radford, *J. Org. Chem.*, **14**, 1089 (1949).
(31) A. Vogel, "Practical Organic Chemistry", Wiley, New York, N.Y., 1956, p 336.
(32) P. T. Izzo and S. R. Safir, *J. Org. Chem.*, **24**, 701 (1959).
(33) M. Tiffenean and Y. Deux, *C. R. Acad. Sci.*, **214**, 892 (1942).
(34) R. O. Robbin, Jr., D. Davidson, and M. T. Bogert, *J. Am. Chem. Soc.*, **57**, 151 (1935).
(35) L. M. Roch, *Ann. Chim. (Paris)*, **6**, 105 (1961).
(36) C. M. Clark and J. D. A. Johnson, *J. Chem. Soc.*, 126 (1962).
(37) R. T. Arnold and P. Veeravagu, *J. Am. Chem. Soc.*, **82**, 5411 (1960).
(38) B. L. Zenitz and W. H. Hartung, *J. Org. Chem.*, **11**, 444 (1946).
(39) J. R. Keneford and J. C. E. Simpson, *J. Chem. Soc.*, 354 (1948).
(40) J. Frejka and H. Zamis, *Cas. Cesk. Lek.*, **63**, 157 (1950); *Chem. Abstr.*, **47**, 2131*e* (1953).
(41) V. V. Devasthale, P. B. Sattur, and K. S. Nargund, *J. Karnatak Univ.*, **1**, 39 (1956); *Chem. Abstr.*, **52**, 8086*c* (1958).
(42) G. Charles and M. Mazet, *C. R. Acad. Sci.*, **87**, 491 (1962).
(43) F. Asinger, H. W. Becker, W. Schafer, and A. Saus, *Monatsh. Chem.*, **97**, 301 (1966).
(44) G. Reddelien, *Ber.*, **43**, 2476 (1910).
(45) C. K. Ingold and S. D. Weaver, *J. Chem. Soc.*, **125**, 1456 (1924).
(46) B. K. Campbell and K. N. Campbell, *J. Org. Chem.*, **9**, 178 (1944).
(47) H. E. Carswell and H. Adkins, *J. Am. Chem. Soc.*, **50**, 235 (1928).
(48) P. Ramart-Lucas and M. J. Hoch, *Bull. Soc. Chim. Fr.*, **3**, 918 (1936).
(49) E. L. Beals and F. A. Gilfillam, *J. Am. Pharm. Assoc.*, **25**, 226 (1926).
(50) G. Reddelien, *Ber.*, **47**, 1364 (1914).
(51) G. S. Forbes and W. G. Leighton, *J. Am. Chem. Soc.*, **52**, 3139 (1930).
(52) J. G. Calvert and J. W. Pitts Jr., "Photochemistry", Wiley, New York, N.Y., 1966, p 787.