# Thermolysis of Tertiary Alkyl Azides[1]

R. A. Abramovitch* and E. P. Kyba

Contribution from the Department of Chemistry, University of Alabama, University, Alabama   35486.   Received June 9, 1973

Abstract: The thermolysis of five tertiary alkyl azides leads to both carbon–nitrogen and nitrogen–nitrogen bond fission in roughly equivalent amounts. Strong evidence for the intermediacy of alkylnitrenes was obtained by the isolation of intramolecular aromatic substitution products, dihydrophenanthridines from $2\text{-}C_6H_5C_6H_4CR_2N_3$ (R = Me and Ph). Other less ideally situated azides lead to no intramolecular aliphatic C–H insertion or aromatic substitution. The implications of a narrow range of migratory aptitudes of quite different groups (aryl and alkyl) to electron-deficient nitrogen are discussed. Pmr and mass spectra of a number of imines along with the mass spectra of the alkyl azides studied are discussed briefly.

The gas[2] and liquid phase[3] thermolyses of alkyl azides have received considerable attention.[4] The decompositions are first order, with activation energies in the range of 38–47 kcal/mol.[2a–c,e,g,3f] Product studies have shown that the predominant process involving N–N bond fission is the loss of nitrogen and rearrangement to an imine.[2,3] Although

$$R_3CN_3 \xrightarrow{-N_2} R_2C{=}NR$$

$$R_3CN_3 \xrightarrow{-N_2} R_2C{-}N \longrightarrow$$

1
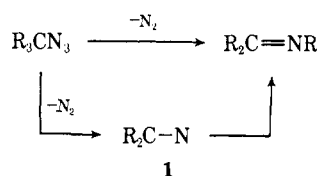
it was often assumed[2,3] that a nitrene intermediate (**1**) was formed, no proof was available to support this view until this work was initiated. The gas phase thermolysis (400°) of methyl and *n*-butyl azide in the presence of cyclohexane or benzene resulted only in traces (<1%) of intermolecular reaction products.[2f] On the other hand, ethyl azide was said to give *ca.* 40% yields of aziridine by intramolecular C–H insertion of ethylnitrene.[2b,e,f] It has recently been reported that an alkylnitrene underwent an intramolecular addition to an olefinic double bond,[5] but the possibility that a triazole intermediate is first formed or that the double bond participates kinetically in the N–N bond breakage,[6] particularly in view of the apparent ease of decomposition, has not been ruled out. It has been suggested[3e] on the basis of the kinetics of the thermal decomposition of triarylmethyl azides of the type

$p\text{-}X\text{-}C_6H_4(C_6H_5)_2CN_3$ that a discrete nitrene is not formed but that a concerted aryl migration–nitrogen elimination occurs. An alternative interpretation of the data has been put forward[4a,d] and this is discussed in more detail later in this paper.

While nitrenes, usually produced by low temperature photolysis in rigid matrices, have been observed by esr,[7] inference for the intermediacy of nitrenes has usually been made either from kinetic studies or from the observation of products (*e.g.*, aromatic addition or substitution or aliphatic C–H insertion) thought to be characteristic of nitrene reactions.[4] In view of the paucity of evidence relating to the mechanism of alkyl azide thermolysis it was of interest to determine whether or not alkyl azides could be so constructed as to allow intramolecular trapping of a possible nitrene intermediate to compete effectively with the almost universal 1,2 shifts leading to imine formation.

Results

The azides **4–6** were synthesized from the corresponding carbinol and HN_3 in chloroform with trichloroacetic acid. Azides **7** and **8** were obtained *via* the tertiary halide and sodium azide in DMF at 90–100°. The former reaction was successful only if at least one aryl group was attached to the tertiary carbon involved in the substitution. When three alkyl groups were present the hydrazoic acid reaction gave rise to olefin in high yield. Indeed, the olefin-forming elimination also predominated in the alkyl halide–sodium azide reaction, but a workable yield (10–20%) of the desired azide was also obtained.

$$\begin{array}{c} R \\ | \\ R'{-}C{-}N_3 \\ | \\ R \end{array}$$
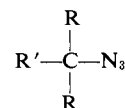
4, R' = $2\text{-}PhC_6H_4$; R = Me
5, R' = $2\text{-}PhC_6H_4$; R = Ph
6, R' = Ph; R = Me
7, R' = R = $n\text{-}C_3H_{11}$
8, R' = $PhCH_2CH_2$; R = Me

Thermolysis of **4–8** was effected under nitrogen in the absence of solvent at 185–220°. The thermolysates were dissolved in benzene, hydrolyzed, and analyzed quantitatively by glc. Preparative glc was used for the isolation of products of the decomposition before

(1) Preliminary reports of some of this work have been published: R. A. Abramovitch and E. P. Kyba, *Chem. Commun.*, 265 (1969); R. A. Abramovitch, J. Court, and E. P. Kyba, *Tetrahedron Lett.*, 4059 (1972).

(2) (a) H. C. Ramsperger, *J. Amer. Chem. Soc.*, **51**, 2134 (1929); (b) J. A. Leermakers, *ibid.*, **55**, 2719 (1933); (c) *ibid.*, **55**, 3098 (1933); (d) F. O. Rice and C. J. Grelecki, *J. Phys. Chem.*, **61**, 830 (1957); (e) G. Geiseler and W. König, *Z. Phys. Chem.*, 277, 81 (1964); (f) W. Pritzkow and D. Timm, *J. Prakt. Chem.*, [4] 32, 178 (1966); (g) M. S. O'Dell, Jr., and B. deB. Darwent, *Can. J. Chem.*, 48, 1140 (1970).

(3) (a) J. K. Senior, *J. Amer. Chem. Soc.*, 38, 2718 (1916); (b) J. H. Boyer and D. Straw, *ibid.*, 74, 4506 (1952); (c) *ibid.*, 75, 1642 (1953); (d) *ibid.*, 75, 2683 (1953); (e) W. H. Saunders, Jr., and J. C. Ware, *ibid.*, 80, 3328 (1958); (f) W. H. Saunders, Jr., and E. A. Caress, *ibid.*, 86, 861 (1964); (g) N. Koga, G. Koga, and J.-P. Anselme, *Can. J. Chem.*, 47, 1143 (1969); (h) A. B. Levy and A. Hassner, *J. Amer. Chem. Soc.*, 93, 2051 (1971).

(4) For recent reviews, see (a) R. A. Abramovitch and E. P. Kyba in "The Chemistry of the Azido Group," S. Patai, Ed., Wiley, London, 1971, p 221; (b) R. A. Abramovitch, *Chem. Soc., Spec. Publ.*, No. 24, 323 (1970); (c) F. D. Lewis and W. H. Saunders, Jr., in "Nitrenes," W. Lwowski, Ed., Wiley, New York, N. Y., 1970, Chapter 3; (d) R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 64, 149 (1964).

(5) J. J. Looker, *J. Org. Chem.*, 36, 1045 (1971).

(6) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).

(7) (a) E. Wasserman, G. Smolinsky, and W. A. Yager, *J. Amer. Chem. Soc.*, 86, 3166 (1964); (b) L. Barash, E. Wasserman, and W. A. Yager, *ibid.*, 89, 3931 (1967).

hydrolysis. In all cases, dark brown tar-like materials were also obtained in addition to the characterizable products.

The results of the thermolysis of 4 are summarized in Scheme I. Olefin 9 had already been obtained in the

Scheme I

9 (62%) 10 (2%)

4

11 (7.5%) 12 (7.6%) 13 (6.5%)
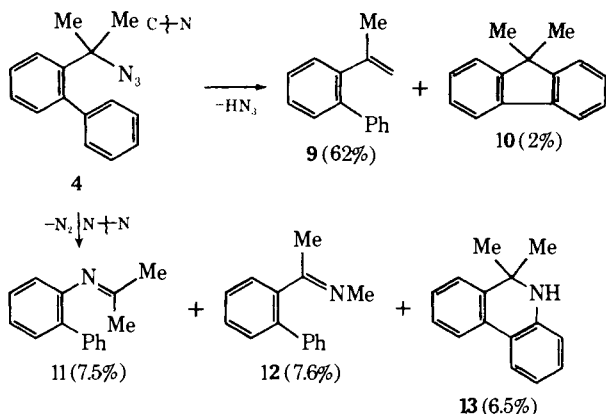
synthesis of 4. 9,9-Dimethylfluorene (10) was prepared by cyclodehydration of 2-(2'-biphenylyl)-2-propanol. The synthesis of imines 11 and 12 has been described elsewhere.[8] Authentic 5,6-dihydro-6,6-dimethylphenanthridine (13) was prepared from 11 with hot polyphosphoric acid. Samples of 6-methylphenanthridine and 2-(2'-biphenylyl)isopropylamine were prepared and shown not to be present among the reaction products.

Thermolysis of 2-biphenylyldiphenylmethyl azide (5) (where olefin formation is not possible) gave the products shown in Scheme II. Authentic 9,9-diphenyl-

Scheme II

14 (5.5%) 15 (16.2%)

5

16 (20.2%) 17 (36.0%) 18 (1.7%)
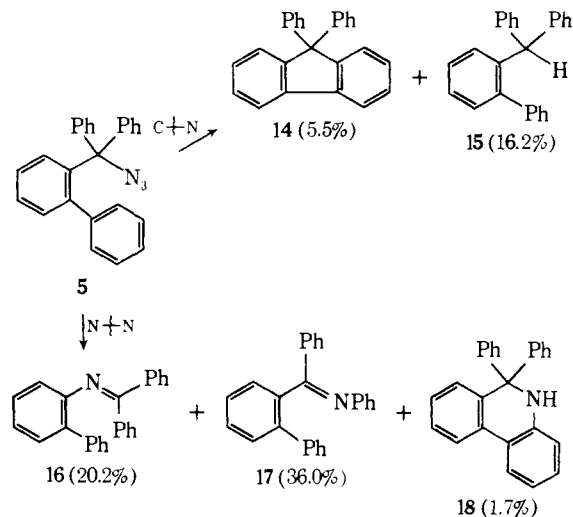
fluorene (14) was prepared by acid-catalyzed cyclodehydration of 2-biphenylyldiphenylcarbinol. 2-Biphenylyldiphenylmethane (15) had the expected spectral properties and was otherwise identical with the known compound.[9] Imines 16 and 17 were obtained from the appropriate amines and ketones using the method of Reddelien.[10] The known[11] dihydrophenanthridine 18 could not be prepared as in the corresponding case of

the 6,6-dimethyl compound 13 by the cyclization of 16 in polyphosphoric acid, but rather was obtained from 6-phenylphenanthridine and phenyllithium.

Decomposition of 2-phenylisopropyl azide (6) took place according to Scheme III. Imines 19 and 20 have

Scheme III

(29%)

6

19 (12.5%) 20 (13.3%) 21 (1.6%)

22
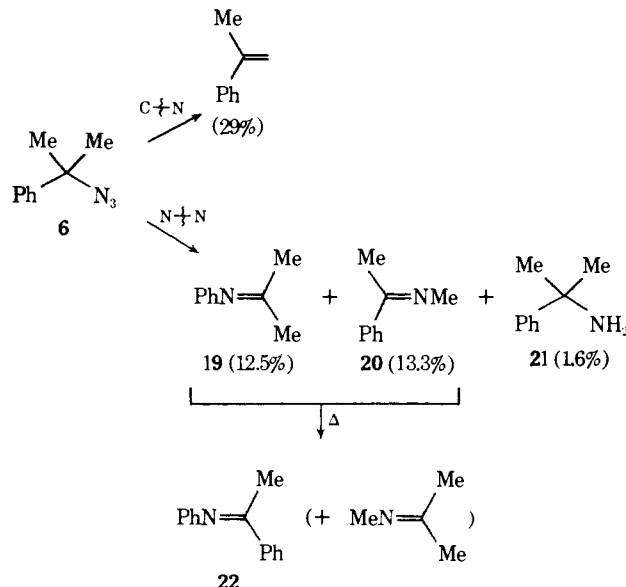
already been described,[8] and 22 was prepared using the Reddelien procedure.[10] It was shown in a control experiment that when 19 and 20 were heated under the conditions of the thermolysis 22 was formed in high yield. Authentic amine 21 was prepared by LiAlH₄ reduction of azide 6.

The thermolysis of azide 7 gave only two major products: the olefin 23 (58.3%) and imine 24 (23.0%).

$$(n\text{-}C_5H_{11})_3CN_3 \xrightarrow{\Delta}$$
7

$$(n\text{-}C_5H_{11})_2C=CHC_4H_9\text{-}n + (n\text{-}C_5H_{11})_2C=NC_5H_{11}\text{-}n$$
23 24

Numerous (ca. 15) minor (<1%) products were formed as indicated by glc analysis, but none disappeared on acid extraction of the benzene solution of the thermolysate, indicating that they did not contain nitrogen (no C–H insertion product). 24 was prepared from 6-undecanone and n-pentylamine.[8]

Scheme IV illustrates the products formed in the

Scheme IV

25 (12.8%) 26 (5.9%) 27 (3.9%)

8

30 28 (8.7%) 29 (7.4%)

(8) E. P. Kyba, *Org. Prep. Proced.*, 2, 149 (1970).
(9) H. H. Hatt, A. Pilgrim, and E. F. M. Stephenson, *J. Chem. Soc.*, 478 (1941).
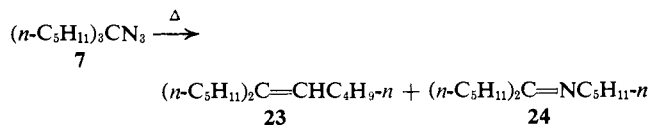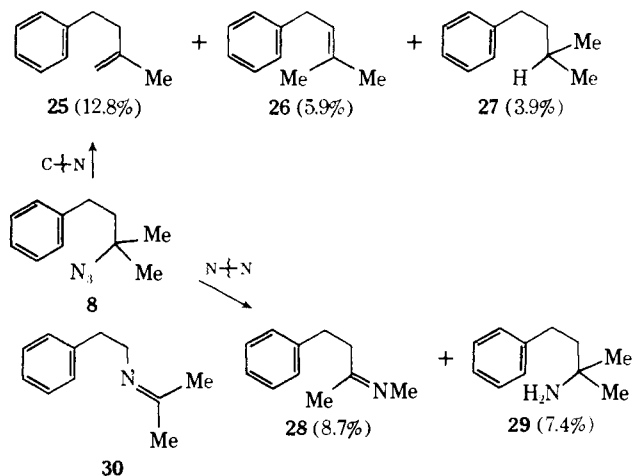(10) G. Reddelien, *Ber.*, 46, 2712 (1913).
(11) H. Gilman and R. D. Nelson, *J. Amer. Chem. Soc.*, 70, 3316 (1948).

thermolysis of **8**. 2-Methyl-4-phenyl-2-butene (**26**) was also obtained from the chloride during the synthesis of **8**, while 2-methyl-4-phenylbutane (**27**) was characterized by its spectroscopic properties. Imines **28** and **30** (the latter not detected even in trace amounts in this reaction; neither was its hydrolysis product 2-phenethylamine) have already been described,[8] while the amine **29** was prepared by a Ritter reaction[12] on 2-methyl-4-phenyl-2-butanol. Since no imine **30** was found an authentic sample was heated under the thermolysis conditions with a fourfold molar excess of azide **8**: no **30** survived this decomposition. The possibility that **30** might be reacting with azide **8** and effectively facilitating the latter's decomposition was studied briefly using a 1:1 molar ratio of imine to azide (a rather unrealistic excess of imine) at various temperatures. The results are summarized in Table I.

Table I. Thermolysis of Azide **8** in the Presence and Absence of Imine **30**. Yield[a] of Azide Remaining after 2 hr

| Temp, °C	8 alone	8 + 30
146	100	97
162	98	90
180	98	78–80

[a] Uncertainty, ±2%.

When **8** and **30** (1:1.3 molar ratio) were heated at 180° until almost all of **8** had decomposed, 39% of **30** survived, and the yield of amine **29** increased from 7.4 to 29% (based on **8**).

Discussion

The formation of dihydrophenanthridines **13** and **18** speaks in support of the intermediacy of alkylnitrenes in these thermolyses. It has been established[13,14] that phenyl groups do not participate in the decomposition of the azido group in 2-azidobiphenyls which leads to carbazoles, and there is no evidence that participation occurs here. 5,6-Dihydro-6,6-dimethylphenanthridine (**13**) formation occurs to a comparable extent with each of the rearrangement processes leading to imines **11** and **12**. It was expected (and was found) that the formation 5,6-dihydro-6,6-diphenylphenanthridine (**18**) would not compete as effectively with rearrangement in view of the greater tendency for an aryl group to migrate to an electron-deficient center than a methyl group (*vide infra*). 1,2-Hydrogen shifts occur even faster, and no dihydrophenanthridine was reportedly formed in the decomposition of 2-biphenylylmethyl azide.[15]

Examination of a model of nitrene **31** shows that the nitrogen atom is very favorably positioned above the benzene ring to effect aromatic substitution. This would not be the case for nitrene **32**, and it does not lead to tetrahydroquinoline formation (Scheme IV). In the hope that the ponderal effect would force an aliphatic C–H group close enough to the nitrene nitrogen so that insertion would compete with 1,2-alkyl migration, tri-(*n*-pentyl)methyl azide (**7**) was decomposed: no evidence of intramolecular C–H
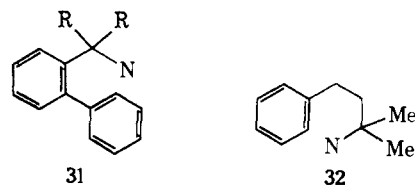

insertion (piperidine, pyrrolidine, or aziridine formation) was obtained. It thus appears that, in the condensed phase at least, conditions must be very favorable for insertion or aromatic substitution to compete with rearrangement of the alkylnitrene.

It is apparent from the results obtained in this work that C–N fission is an important mode of decomposition of tertiary alkyl azides, even when, as with **5**, β-elimination is not possible. Since previous workers[3f] had not reported such a process for 2-phenylisopropyl azide (**6**) its thermolysis was studied and was found to give appreciable amounts (29%) of α-methylstyrene. Either a heterolytic or homolytic C–N bond cleavage can be envisaged. Heterolytic cleavage to a tertiary carbanion and N_3^+ can readily be ruled out on energetic grounds.[16] Although cleavage to give a tertiary carbenium ion and N_3^- is attractive, a number of results speak against the exclusive operation of such a process, particularly in the absence of a polar solvent. Thus the formation of the hydrocarbons **15** and **27** (Schemes II and IV) is hard to account for in this way. It is known that the 2-biphenylyldiphenylcarbenium ion (**33**) cyclizes quantitatively to 9,9-diphenylfluorene (**14**).[17] Since **15** is formed in about three times the amount of **14** an intermediate other than **33** must be giving rise to **15**. Similarly, carbenium ion **34** is known to cyclize to 1,1-dimethylindene (**35**) in good yield,[18]
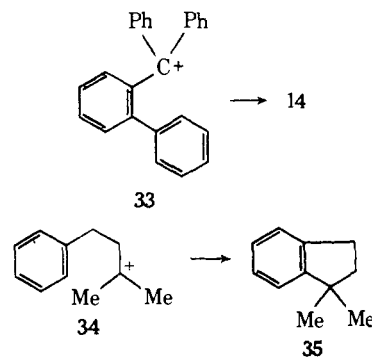
but no **35** could be detected in the decomposition of **8** (Scheme IV). A more attractive sequence of events is outlined in Scheme V in which C–N homolysis leads to

Scheme V
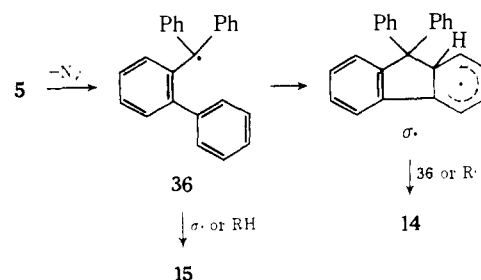
(12) J. J. Ritter and P. P. Minieri, *J. Amer. Chem. Soc.*, **70**, 4045 (1948); J. J. Ritter and J. Kalish, *ibid.*, **70**, 4048 (1948).

(13) L. K. Dyall and J. E. Kemp, *J. Chem. Soc. B*, 976 (1968).

(14) P. A. S. Smith and J. H. Hall, *J. Amer. Chem. Soc.*, **84**, 480 (1962).

(15) B. Coffin and R. F. Robbins, *J. Chem. Soc.*, 1252 (1965).

(16) B. L. Evans, A. D. Yoffe, and P. Gray, *Chem. Rev.*, **59**, 515 (1959).

(17) H. Hart and E. A. Sedor, *J. Amer. Chem. Soc.*, **89**, 2342 (1967).

(18) M. T. Bogert and D. Davidson, *J. Amer. Chem. Soc.*, **56**, 185 (1934).

the radical **36**, and thence to **14** and **15**. It might be noted that, in contrast to thermolysis, photolysis of the azides studied here led almost exclusively to N–N bond fission.[19a]

In view of the results obtained in the thermolysis of azide **8** in the absence and the presence of added imine **30** it seems that, in cases where much tar is formed in the thermolyses and one of the expected imines is not observed, migratory ratio data must be viewed with some caution. It must be emphasized, however, that the amounts of **30** added are *ca.* 10 times more than would be present at the *end* of the reaction were it not consumed. With the much smaller amounts of **30** expected its effect upon the decomposition of **8** (Table I) would be small indeed. On the other hand, if **30** is formed in low yield in this thermolysis it would not be expected to survive, so that it is not surprising, in retrospect, that none was isolated. The amine **29** can arise either by hydrogen abstraction by the free nitrene or, at least in part, from a reaction between **30** and **8**. This could be a 1,3-dipolar addition of azide to azomethine, followed by cleavage and hydrolysis to give **29**. This was not investigated further. The very small amounts of amine **21** obtained from **5** (Scheme III) could arise similarly. Since this side reaction does not constitute a problem in the cases of the thermolysis of **4**, **5**, **6**, and **7** an analysis of the migratory ratio appears to be warranted. In particular, a consideration of the statistically corrected aryl/Me migratory ratios in the decompositions of **6** and **4** reveals that these are remarkably small: Ph/Me = 1.9 and o-PhC₆H₄/Me = 2.0, respectively.[19b] This may be contrasted with the behavior of free alkyl radicals when only phenyl, but not methyl, migration occurs to the reaction center.[20] Also, in the formolysis of neophyl derivatives, in which the developing positive charge is delocalized over the participating migrating groups, the Ph/Me migratory ratios were 10³ or greater.[21] The latter values are in closer concordance with those found[22] in the triethyl phosphite deoxygenation of the corresponding tertiary alkyl nitroso derivatives **37** (Ph/Me > 160; 2-PhC₆H₄/Me > 1600) for which a fast reaction of phosphite with nitroso compound was suggested followed by a slower, anchimerically assisted elimination of triethyl phosphate and migration (Scheme VI). Only when a "hot" carbenium ion is generated does methyl migration compete effectively with phenyl migration.[23] The Ph/Me migration ratio to a carbene center has been found to be about 10.[24] The migratory ratios observed in this work confirm the conclusion reached above on the basis of the observation of some aromatic

(19) (a) R. A. Abramovitch and E. P. Kyba, *J. Amer. Chem. Soc.*, **93**, 1537 (1971). (b) It is significant also that these two decompositions predict an o-PhC₆H₄/Ph migratory ratio of 2.0/1.9 = 1.05, which compares well with the observed ratio of 1.1 (Scheme II, 16/0.5 × 17). This is in marked contrast to the photochemical decompositions of these azides, in which nitrenes are thought not to be involved.[19a] Thus, the same considerations as above would lead to a predicted photochemical migratory ratio o-PhC₆H₄/Ph which is 2.2 times larger than is actually observed.

(20) (a) F. H. Seubold, Jr., *J. Amer. Chem. Soc.*, **75**, 2532 (1953). (b) A full discussion of these migratory aptitudes may be found in ref 4a.
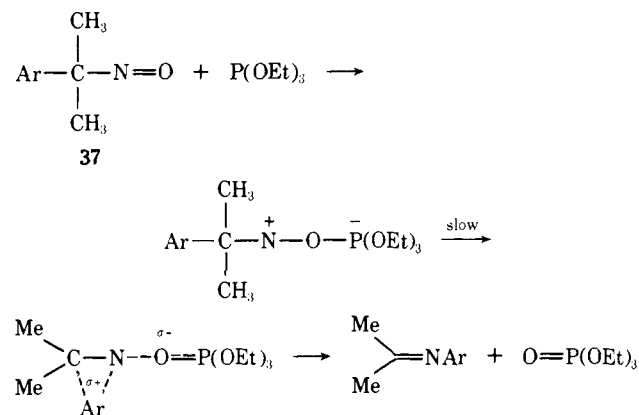
(21) W. H. Saunders, Jr., and R. H. Paine, *J. Amer. Chem. Soc.*, **83**, 882 (1961).

(22) R. A. Abramovitch, J. Court, and E. P. Kyba, *Tetrahedron Lett.*, 4059 (1972).

(23) D. J. Cram and J. E. McCarty, *J. Amer. Chem. Soc.*, **79**, 2866 (1957).

(24) H. Phillip and J. Keating, *Tetrahedron Lett.*, 523 (1961).

Scheme VI

substitution, namely that free alkylnitrenes are formed in these thermolyses and that migration occurs without participation in the nitrogen elimination. It is significant that an o-phenyl group has only a minor effect on the migratory aptitude, as seen from the thermolysis of **5** (o-PhC₆H₄/Ph = 1.1), again suggesting a high energy, relatively nondiscriminating, intermediate. In the thermolysis of triarylmethyl azides to give benzophenone anils the migratory ratios varied from p-Me₂NC₆H₄/Ph = 6.7 to p-NO₂C₆H₄/Ph = 0.2.[3e] Again, these differences are small compared to those in which assisted decomposition–migration occurs, as has been discussed elsewhere.[4a,d] We conclude, therefore, that the thermolysis of tertiary alkyl azides leads to an electrophilic singlet nitrene intermediate.

Nmr Spectra of Imines. During the course of the above work much spectroscopic data were accumulated on the imines and azides prepared, and some of these will be discussed.

Several nmr studies of imines bearing at least one alkyl group have been reported.[25] In general, it has been found that a methyl group syn to the lone pair of electrons on nitrogen (position a in **38**) resonates at
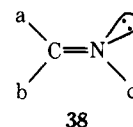
ca. 0.2 ppm lower field than the CH₃ protons do at position b, when the N substituent at d is an alkyl group.[25a,c,d,26] The N-isopropylideneamines studied in the present work show the same general trend except that there is a larger chemical shift difference when d is aryl or phenethyl (Table II). The downfield absorption (δ 2.00) of the methyl group syn to the lone pair is about the same as when d is alkyl, but the group anti to the lone pair is significantly shielded. This can be

(25) (a) H. A. Staab, F. Vogtle, and A. Mannschrete, *Tetrahedron Lett.*, 697 (1965); (b) G. A. Olah and P. Kreienbühl, *J. Amer. Chem. Soc.*, **89**, 4756 (1967); (c) D. A. Nelson and R. L. Atkins, *Tetrahedron Lett.*, 5197 (1967); (d) T. Yonezawa, I. Morishima, and K. Fuktua, *Bull. Chem. Soc. Jap.*, **41**, 2297 (1968); (e) W. B. Jennings and D. Boyd, *J. Amer. Chem. Soc.*, **94**, 7188 (1972); (f) J. Bjørgo, D. R. Boyd, and C. G. Watson, *Tetrahedron Lett.*, 1747 (1972); (g) D. R. Boyd, C. G. Watson, W. B. Jennings, and D. M. Jerina, *J. Chem. Soc., Chem. Commun.*, 187 (1972).

(26) Deshielding of the pyridine α protons (relative to the β and γ protons) has been attributed[27] to the magnetic anisotropy of the N atom lone pair and to the local dipole moment of the C=N bond. In **38**, the latter should affect a and b equally.

(27) V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, **60**, 248 (1964).

Table II. Chemical Shifts (Relative to TMS) of Some
N-Isopropylideneamines in CCl_4 Solutions

	δ (ppm)	
d	syn-CH_3 (a)	anti-CH_3 (b)
t-Bu	1.85	1.85
Ph (19)	2.00	1.63
o-PhC_6H_4 (11)	1.80	1.31
$PhCH_2CH_2$ (30)	1.80	1.49

explained by assuming that the aryl group is not co-planar with the imine linkage (in **11** and **19**) so that the *anti*-CH_3 group (b) is in the shielding volume of the phenyl ring. Recent evidence indicates that even when b = H, an N-phenyl group is not in the same plane as the C=N.[28] That the *syn*-CH_3 groups in **11** and **30** resonate at somewhat higher field than they do in a purely aliphatic amine might be attributed to slight shielding by the phenyl groups (but not as strong as that of the closer *anti*-CH_3 (b) group). When d = t-Bu, only one methyl resonance is observed for *both* a and b; this may be due to severe nonbonded interactions between the b-CH_3 and the *tert*-butyl group, which could raise the ground-state energy sufficiently such that the barrier to the degenerate syn–anti conversion could be low enough for the process to be fast on the nmr time scale.[29] Such an effect has recently been determined quantitatively with a pair of imines p-$NO_2C_6H_4C(Ph)$=NR.[25e] It was found that the energy barrier to inversion (syn–anti isomerization) for R = *tert*-butyl was 5.7 kcal/mol *lower* than that for R = Me.

Scheme VII illustrates the methyl resonances of several N-ylidenemethylamines. Syn–anti isomerism is observed in these cases, and the amount of each isomer can be estimated by nmr and is given in Scheme VII for solutions in CCl_4 at ambient temperatures. As can be seen from Scheme VII, the anti coupling constants (*ca.* 1.4 Hz) are larger than the syn (0.7–1.0 Hz),[25b,c,d] in agreement with those observed for the olefinic counterparts of imines.[30] The chemical shifts can be rationalized as have those of the N-isopropylideneamines above.

The position of equilibrium for imines **20**, **28**, and **39** is readily explained on the basis of less steric hindrance for the N-methyl group when it is syn to the methyl group than to the other group, as can be readily confirmed by consideration of molecular models. On the other hand, when the other group is 2-biphenylyl the opposite effect is observed. If CPK space-filling models of **20a** and **20b** are examined, one finds that the phenyl group in **20a** can exist essentially coplanar with the imine linkage, whereas at best it is about 45° out of coplanarity with the imino group in **20b**. The replacement of an ortho-hydrogen atom by a phenyl group in **20b** (→**12b**) merely immobilizes the nearly perpendicular imino group to a small extent. On the

(28) (a) A. Van Putten and J. W. Pavlik, *Tetrahedron*, **27**, 3007 (1971); (b) M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Amer. Chem. Soc.*, **93**, 586 (1971).
(29) For leading references to such processes, see R. M. Moriarity, C.-L. Yeh, K. C. Ramey, and P. W. Whitehurst, *J. Amer. Chem. Soc.*, **92**, 6360 (1970).
(30) S. Sternhell, *Pure Appl. Chem.*, **14**, 15 (1964).

Scheme VII. Chemical Shifts (δ in ppm from TMS), Homoallylic Coupling Constants, and Percentages of Syn and Anti Isomers of Some N-Ylidenemethylamines (15% w/v in CCl_4) at Ambient Temperatures
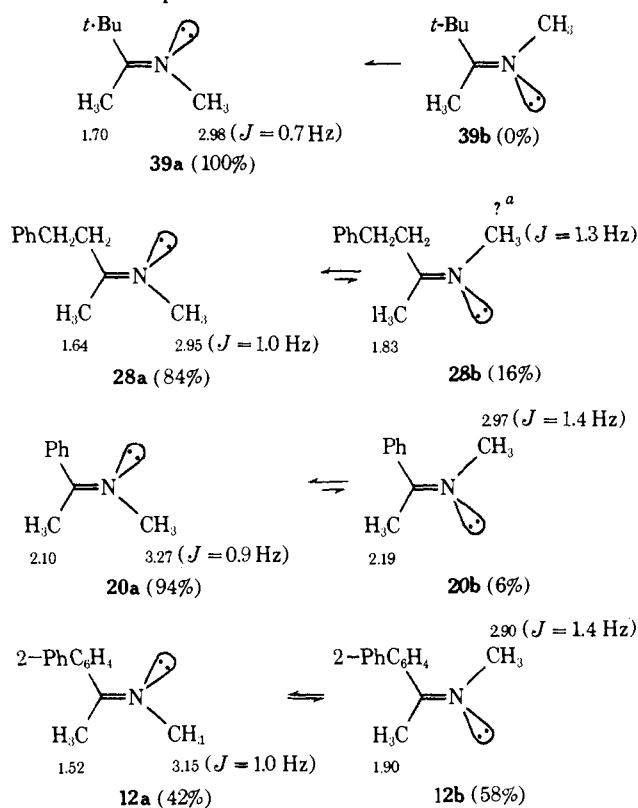
a The N–CH_3 resonance could not be distinguished from the phenethylmethylene resonance.

other hand, the same substitution in **20a** (→ **12a**) has a drastic effect in that the C=N linkage is now forced completely out of coplanarity with the attached phenyl ring. The net result of this is to make **12a** and **12b** nearly equal in energy (*ca.* 0.2 kcal/mol difference observed). In order to explain the slight energetic preference for **12b** minor effects such as librational freedom of the C=N group and rotational freedom of the methyl groups in **12a** and **12b** would have to be considered. Interestingly, an o-MeO substituent has virtually the same effect as an o-Ph on the syn–anti equilibium. An alternate explanation involving "n–π repulsive interactions"[25f] has been postulated and is being tested by one of us.

The proton chemical shifts for N-(6-undecylidene)-1-pentylamine (**24**) in CCl_4 solution are shown below.
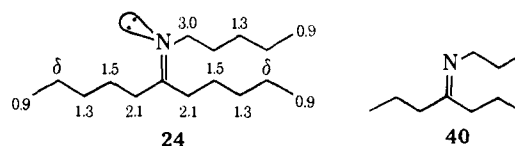
The ratio of the areas for the proton peaks was expected to be $\alpha_N:\alpha_C:(\beta + \gamma + \delta):\epsilon = 2:4:18:9$. The observed ratio was 2:4:16:11 which is well beyond the limit of the experimental error in our measurement of peak areas. Species **24** was shown to be a pure compound by glc, ir, mass spectral, and elemental analysis. We conclude that one pair of the β, γ, or δ methylene protons is in a conformation in which it is anisotropically shielded[28] so that its signal appears under the

methyl envelope. The δ-methylene protons are the most likely candidates as we have found that N-(4-heptylidene)-1-propylamine (40) shows no such effect. Molecular models confirm this suggestion, but more work is needed to establish which of the three δ-methylene groups is the one actually shielded.

Mass Spectra of Imines. These follow the pattern of examples in the literature,[31] the fragmentation being dominated by the presence of the imino group in which the nitrogen atom stabilizes the positive charge. This is illustrated below for N-(α-methylbenzylidene)-methylamine (20). The mass spectral data for ten
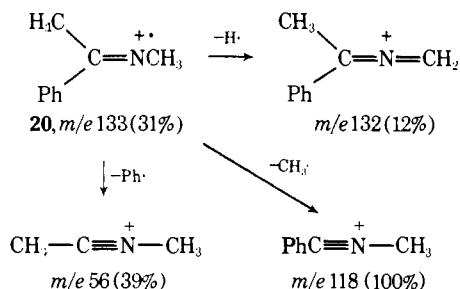

imines studied here are given in the Experimental Section.

Mass Spectra of Alkyl Azides. Only one paper has appeared on this subject, and it deals with three substituted triarylmethyl azides (41; X = CH₃, Cl, and
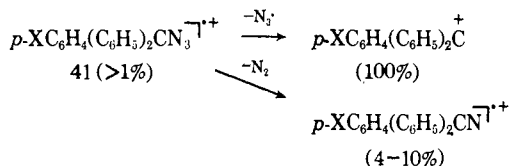
NO₂).[32] Fragmentation was found to be dominated by C–N cleavage to give the carbenium ion as base peak.

The mass spectra of the alkyl azides studied in this work are given in the Experimental Section. These may be divided conveniently into three groups. Triphenylmethyl azide and 2-biphenyldiphenylmethyl azide (5) showed no molecular ion, C–N bond cleavage being predominant and N–N bond cleavage minor, in accord with the previous scheme.[32] One difference was observed with 5, namely that the base peak was due
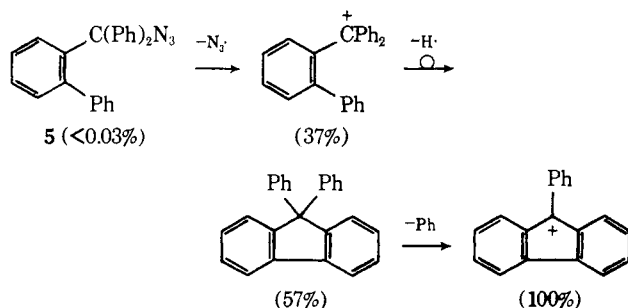
to M − N₃ − Ph − H, presumably the 9-phenylfluorenyl cation.

The second group of azides includes α-methylbenzyl azide, 2-phenylisopropyl azide (6), and 2-(4'-biphenyl-

yl)isopropyl azide, each of which has only one aryl group attached to the carbon bearing the azide group, and each showing an M⁺ ion (0.5–5% relative abundance). C–N bond cleavage is still the primary mode of fragmentation. 2-(2'-Biphenylyl)isopropyl azide (4) does not show an M⁺ peak, however, and gives the 9-methylfluorenyl cation as the base peak.

The effect of varying the method of sample introduction into the mass spectrometer[33] was studied with azide 4. It was found that the use of the heated inlet system (ca. 200°) gave a mass spectrum quite different from that obtained using the direct probe inlet at ambient temperatures.[34] In fact, the spectrum obtained using the heated inlet system can be rationalized as a composite of the possible thermolysis products (Table III).

Table III. Relative Abundance of Major Peaks in the Mass Spectra of Azide (4) and Its Possible Thermolysis Products[a]

m/e	ArC-(Me)=CH₂	ArN=CMe₂	ArC-(Me)=NMe	Azide 4 heated inlet[b]	Azide 4 direct inlet
209		28	19	37	1
208		4	100	74	2
195	6	17	4	14	16
194	37	100	26	91	67
180	15				16
179	100		9	37	100
178	52		7	19	57
165	9		10	19	13
152	9	32	11	36	18
151	5	8	5	13	9
77	4	4	3	18	6
76	8	15	4	21	12
56			22	68	
43				100	18
42				32	

[a] Ar = 2-biphenylyl. [b] The instrument used was a CEC 21-104 single focussing mass spectrometer, with an ionization potential of 70 eV and an accelerating voltage of 1.2 keV.

The four azides studied which had no aryl group attached to the α-carbon atom did not exhibit parent ions, even at the lowest possible ionization potential, and the M − N₂ and M − N₃· fragments appear only in low relative abundance in all four cases.

Experimental Section

General. Melting points are uncorrected. Nmr spectra were recorded on a Varian Associates HA-100 spectrometer using tetramethylsilane as internal standard, and mass spectra on a CEC 21-104 spectrometer. Gas chromatographic analyses were carried out on a Varian-Aerograph 1700 gas chromatograph. Preparative gas chromatography was effected on a Nester-Faust Prep-kromatic 850 instrument.

Commercially available reagents and solvents were usually reagent grade and distilled or recrystallized prior to use. Light petroleum refers to the fraction bp 30–60° unless otherwise stated. Basic alumina for all column chromatography was activated by heating at 375° for 12 hr, followed by cooling in a vacuum desiccator. Molecular sieves [Davison (Fisher Scientific Co.), type 4A, grade 514, 8–12 mesh] were activated at 375° for 12 hr, cooled, and stored in a vacuum desiccator.

2-Acetylbiphenyl, bp 100–105° (55 μ) (lit.[35] bp 104–105° (1 Torr)), was prepared in 87% yield from methyllithium and 2-biphenylycarboxylic acid.

(31) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 388–394.

(32) R. M. Moriarity and A. M. Dirkien-Konasiewicz, Tetrahedron Lett., 4123 (1966).

(33) C. Larsen and P. Jakobsen, Acta Chem. Scand., 24, 1445 (1970).

(34) Azide 4 begins to decompose at 185°.

(35) E. Campaigne and W. B. Reid, Jr., J. Amer. Chem. Soc., 68, 1663 (1946).

2-(2′-Biphenylyl)-2-propanol, mp 71–72° (from light petroleum) (lit.[36] mp 73°), was prepared in 55% yield from 2-acetylbiphenyl and methylmagnesium iodide.

2-Phenyl-2-propanol, mp 31–33°, was similarly prepared from PhLi and acetone.

2-(2′-Biphenylyl)isopropyl Azide (4). A solution of the 2-propanol (5.14 g, 24.2 mmol) in CHCl₃ (25 ml) was added in one portion to trichloroacetic acid (9.0 g, 55 mmol) in a 2.2 M solution of HN₃ in CHCl₃ (200 ml). The resulting solution was allowed to stand at room temperature for 24 hr, then washed with 2% aqueous sodium carbonate (5 × 100 ml), dried (MgSO₄), and concentrated. The resulting oily residue was chromatographed on alumina (500 g). Elution with light petroleum (1.5 l.) gave 2-(2′-biphenylyl)propene (9) (1.79 g): bp 63–64° (10 μ) (lit.[37] bp 149° (20 mm)); ir (liquid film) 1630 (C=C) and 906 cm⁻¹ (vinyl CH₂); nmr (CCl₄) τ 2.85 (m, 9), 5.06 (m, 2), and 8.42 (d of d, J_1 = 0.8 and J_2 = 0.6 Hz, 3); ms (70 eV) m/e 194 (M⁺). Elution with light petroleum–ether (97:3, v/v) (1.5 l.) gave a colorless oil (2.77 g) contaminated with **9**. This fraction was chromatographed on alumina twice, using the eluents as described above in the same amounts. The purified liquid was then distilled under vacuum to give the azide as a colorless oil (1.86 g, 32%): bp 85° (20 μ); ir (liquid film) 2100 (N₃ asym. str.) and 1250 cm⁻¹ (N₃ sym. str.); uv (cyclohexane) λmax 251, 290, 301 nm (ε 820, 86, 123); nmr (CCl₄) τ 2.77 (m, 9) and 8.60 (s, 6).

Anal. Calcd for C₁₅H₁₅N₃: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.27; H, 6.42; N, 17.93.

5,6-Dihydro-6,6-dimethylphenanthridine (13). N-Isopropylidene-2-aminobiphenyl[8] (186 mg, 0.89 mmol) and polyphosphoric acid (4.0 g) were heated at 165–170° with vigorous stirring for 2 hr. Water (4.5 ml) was added to the cooled reaction mixture which was then made basic (4 M NaOH) and extracted with ether (3 × 30 ml). The ethereal extracts were dried (MgSO₄) and concentrated and the residue was chromatographed on alumina (50 g). Elution with light petroleum–benzene (7:3, v/v) gave a white solid (87 mg), mp 101–102°. Four recrystallizations from aqueous methanol gave **13** (50 mg, 27%): mp 103–104.5°; ir (KBr) 3350 cm⁻¹ (N–H); nmr (CCl₄) τ 3.0 (m, 8), 6.58 (s, 1), and 8.67 (s, 6); ms (70 eV) m/e 209 (M⁺).

Anal. Calcd for C₁₅H₁₅N: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.04; H, 7.15; N, 7.07.

6-Methylphenanthridine was prepared by the method of Morgan and Walls.[38]

2-(2′-Biphenylyl)isopropylamine. 2-(2′-Biphenylyl)isopropyl azide (2.69 g, 11.3 mmol) in dry ether (40 ml) was treated with a 2 M ethereal solution of lithium aluminum hydride (12 ml). [The first portion of the hydride solution was added dropwise, as there is an induction period (*ca.* 5 min) in the reaction, after which gas evolution is rapid. After gas evolution commenced the remainder of the hydride solution was added more rapidly.] The resulting solution was boiled under reflux for 16 hr and cooled, and ethanol (6.8 ml) was added dropwise. Addition of water (10 ml) coagulated the fine white precipitate. The ethereal solution was filtered, dried (MgSO₄) and concentrated. The residue was dissolved in benzene (40 ml) and hydrogen chloride was bubbled into the solution. The white solid was filtered, dissolved in boiling water (60 ml), and treated with activated charcoal. Crystallization gave the amine hydrochloride (1.65 g, 58%), mp >330°.

Anal. Calcd for C₁₅H₁₈NCl: C, 72.71; H, 7.32. Found: C, 72.63; H, 7.36.

The hydrochloride was suspended in water (10 ml), and the aqueous solution was made basic (NaOH) and extracted with ether (2 × 20 ml). The ethereal extracts were combined, dried, and concentrated. The residue was recrystallized from pentane to give 2-(2′-biphenylyl)isopropylamine (0.98 g, 41%): mp 39.5–41°; ir (KBr) 3360 and 3280 cm⁻¹ (NH₂); nmr (CCl₄) τ 2.41 (m, 1), 2.78 (m, 8), 8.72 (s, 6), and 8.87 (s, 2, collapses on addition of D₂O); ms (70 eV) m/e (rel intensity) 211 (M⁺, 2), 196 (M⁺ − Me, 100).

2-Phenylisopropylamine (21) was similarly prepared (46% yield) from the corresponding azide and had bp 196–197° (762 mm); ir (film) 3370 and 3290 cm⁻¹ (NH₂).

2-Biphenylyldiphenylmethyl Azide (5). 2-Biphenylyldiphenylcarbinol[18] (16.0 g, 44.3 mmol) was dissolved in a 2 M solution of hydrazoic acid in chloroform (400 ml) and allowed to stand at room

temperature for 14 days. The solution was then extracted with 4% aqueous sodium bicarbonate until the extracts remained basic (5 × 300 ml); it was dried and concentrated to give a yellow oily residue (18.4 g). Light petroleum (100 ml) was added to the residue and the solid which crystallized was filtered and recrystallized from light petroleum to give the azide **5** (13.9 g, 87%): mp 116–118°; ir (KBr) 2110 (N₃ asym. str.) and 1280 (N₃ sym str.); uv (C₆H₁₂) no distinct λmax, ε at 290, 270, 250, and 220 nm, 1.4 × 10², 1.4 × 10³, 3.8 × 10³, and 4 × 10⁴; nmr (CCl₄) τ 2.9 (m, 17) and 3.4 (m, 2).

Anal. Calcd for C₂₅H₁₉N₃: C, 83.07; H, 5.30. Found: C, 83.22; H, 5.29.

9,9-Diphenylfluorene (14), mp 224–226° (lit.[39] mp 222°), was prepared in quantitative yield from 2-biphenylyldiphenylcarbinol and boiling 90% aqueous formic acid.

2-Phenylbenzophenone, mp 86–88° (lit.[9] mp 91–92°), was prepared in 61% yield from 2-biphenylylcarboxylic acid and phenyllithium: ir (KBr) 1660 cm⁻¹ (C=O); ms (70 eV) m/e 258 (M⁺).

2-Phenylbenzophenone Anil (17). 2-Phenylbenzophenone (997 mg, 3.86 mmol), aniline (2.43 g, 26.2 mmol), and aniline hydrobromide (101 mg, 0.58 mmol) were heated in the absence of solvent under reflux under nitrogen for 42 hr. The deep purple mixture was extracted with pentane (50 ml), dried, and concentrated to give a brownish residue (1 g). This was distilled under vacuum to give a bright yellow glass (0.45 g), bp 180–185° (20 μ), which was crystallized from ethanol to give the imine **17** as a yellow solid (200 mg, 15%): mp 90–92° (lit.[9] mp 91–92°); ir (KBr) 1620 cm⁻¹ (C=N); ms (70 eV) m/e 333 (M⁺).

N-Benzhydrylidene-2-aminobiphenyl (16). Benzophenone (5.46 g, 30 mmol), 2-aminobiphenyl (10.2 g, 60 mmol), and 48% aqueous hydrobromic acid (0.1 ml) were heated at 180° for 3.5 hr. The mixture was cooled, absolute ethanol (15 ml) added, and the resulting solution was stored in the refrigerator overnight. The yellow solid which crystallized was filtered and recrystallized twice from absolute ethanol to give the imine (**16**) as bright yellow needles (2.5 g, 25%): mp 120–121°; ir (KBr) 1620 cm⁻¹ (C=N); nmr (CCl₄) τ 2.45 (m, 2), 2.9 (m, 15), and 3.4 (m, 2); ms (70 eV) m/e 333 (M⁺).

Anal. Calcd for C₂₅H₁₉N: C, 90.06; H, 5.74. Found: C, 90.34; H, 5.94.

5,6-Dihydro-6,6-diphenylphenanthridine (18). This was prepared by the addition of phenyllithium (200 mmol) to 6-phenylphenanthridine[38] (6.55 g, 25.7 mmol) in dry ether. The solid obtained after work-up was recrystallized from light petroleum (bp 60–100°) to give the dihydrophenanthridine **18** as light yellow needles (1.65 g, 19%): mp 157–159° (lit.[11] mp 147.5–148°); ir (KBr) 3380 and 3370 cm⁻¹ (N–H); ms (70 eV) m/e 333 (M⁺).

Anal. Calcd for C₂₅H₁₉N: C, 90.06; H, 5.74. Found: C, 90.08; H, 5.78.

Tris-n-pentylcarbinol. A solution of n-pentylmagnesium bromide (541 mmol) in dry ether (300 ml) was added to 6-undecanone (61.5 g, 362 mmol) in dry ether at such a rate that gentle reflux was maintained. The reaction mixture was boiled under reflux for 17 hr and cooled in an ice bath, and 2 M hydrochloric acid (200 ml) was added carefully. The two layers were separated, and the ethereal extract was washed with water (3 × 200 ml), dried, and concentrated to give a colorless oil (87 g). Vacuum distillation gave two fractions. The first (17.6 g, 21%), bp 120–130° (40 mm), was starting ketone. The second was the carbinol (54.1 g, 87%): bp 90–95° (20 μ); ir (film) 3450 cm⁻¹ (O–H, bonded); nmr (CCl₄) τ 8.35 (s, 1, disappears on addition of D₂O), 8.72 (m, 24), and 9.11 (m, 9).

Anal. Calcd for C₁₆H₃₄O: C, 79.26; H, 14.13. Found: C, 78.92; H, 14.14.

6-(n-Pentyl)-5-undecene (23). A mixture of tri-n-pentylcarbinol (1.14 g, 4.69 mmol) and 30% aqueous sulfuric acid (2 ml) was boiled under reflux for 5 hr. Water (10 ml) and ether (10 ml) were added and the two layers were separated. The ethereal portion was extracted with water (2 × 10 ml), dried, and concentrated to give a colorless liquid which was distilled under vacuum to give 6-(n-pentyl)-5-undecene (**23**) as a colorless oil (0.51 g, 48%): bp 65–70° (10 μ); nmr (CCl₄) τ 5.00 (t, J = 7 Hz, 1), 8.08 (m, 6), 8.85 (m, 16), and 9.14 (m, 9); ms (70 eV) m/e 224 (M⁺).

Anal. Calcd for C₁₆H₃₂: C, 85.63; H, 14.37. Found: C, 85.83; H, 14.21.

Tri-n-pentylmethyl Chloride. Thionyl chloride (11.2 g, 94 mmol) in dry chloroform (20 ml) was added dropwise to tri-n-pentylcarbinol (21.1 g, 87.2 mmol) in dry chloroform (35 ml). The solution was stirred for 15 min until gas evolution had ceased, and

(36) M. Anchell and A. H. Blatt, *J. Amer. Chem. Soc.,* **63,** 1948 (1941).

(37) I. A. Goodman and P. H. Wise, *J. Amer. Chem. Soc.,* **72,** 3076 (1950).

(38) L. P. Morgan and G. T. Walls, *J. Chem. Soc.,* 2447 (1931).

(39) F. Ullman and R. von Wurstenburger, *Ber.,* **38,** 4105 (1905).

then concentrated. The residue was dissolved in ether (300 ml) and washed with water (2 × 300 ml), dried, and concentrated to give a yellow oil (21.6 g), which was distilled under vacuum to give the chloride (20.0 g, 88%): bp 98–103° (15 μ); nmr (CCl₄) τ 8.3 (m, 6), 8.7 (m, 18), and 9.10 (m, 9).

Anal. Calcd for C₁₆H₃₃Cl: C, 73.66; H, 12.75. Found: C, 73.69; H, 12.64.

Tri-*n*-pentylmethyl Azide (7). A mixture of tri-*n*-pentylmethyl chloride (16.6 g, 63.9 mmol), sodium azide (8.3 g, 128 mmol), and *N,N*-dimethylformamide (170 ml) was stirred vigorously at 95–100° for 60 hr. The mixture was extracted with pentane (2 × 150 ml); the combined pentane extracts were washed with water (3 × 150 ml), dried, and concentrated to give a light yellow oil (15 g). Elution with light petroleum (1.0 l.) gave a colorless liquid (11.9 g, 83%); ir and mass spectrum identical with those of olefin **23.** Elution with more light petroleum (500 ml) gave a colorless oil (1.5 g) which was chromatographed again on alumina (150 g). Elution with light petroleum (250 ml) gave **23** (0.24 g), and further elution with the same solvent (100 ml) gave a colorless oil (1.2 g), which was distilled under vacuum to give the azide **7** as a colorless liquid (1.1 g, 6%): bp 95–100° (20 μ); ir (film) 2100 (N₃ asym. str.) and 1255 cm⁻¹ (N₃ sym. str.); uv (C₆H₁₂) λ_max 285 nm (ε 25); nmr (CCl₄) τ 8.7 (m, 24) and 9.1 (m, 9).

Anal. Calcd for C₁₆H₃₃N₃: C, 71.85; H, 12.45. Found: C, 71.86; H, 12.27.

N-(6-Undecylidene)-1-pentylamine (24). 6-Undecanone (844 mg, 5.0 mmol), *n*-pentylamine (870 mg, 10 mmol), and 4A molecular sieves (1.5 g) were heated at 100° for 4 hr. The mixture was filtered and distilled under vacuum to give the imine **24** (560 mg, 47%): bp 61–62° (15 μ); ir (film) 1660 cm⁻¹ (C=N); nmr (CCl₄) τ 7.0 (m, 2), 7.9 (m, 4), 8.7 (m,16), and 9.1 (m, 11); ms (70 eV) *m/e* 239 (M⁺).

Anal. Calcd for C₁₆H₃₃N: C, 80.40; H, 13.92. Found: C, 80.17; H, 13.99.

2-Chloro-2-methyl-4-phenylbutane. Thionyl chloride (27.4 g, 230 mmol) in chloroform (40 ml) was added dropwise to 2-methyl-4-phenyl-2-butanol[40] (32.6 g, 199 mmol) in dry chloroform (55 ml). The resulting solution was stirred for a further 0.5 hr after all the gas evolution had subsided, and then concentrated. The residue was dissolved in ether (150 ml), extracted with water (3 × 100 ml), dried, and concentrated to give the chloride (27.9 g, 77%): bp 62–66° (15 μ); ir (film) 1380 and 1360 cm⁻¹ (*gem*-dimethyl); nmr (CCl₄) τ 2.92 (m, 5), 7.30 (m, 2), 8.06 (m, 2), and 8.45 (s, 6).

Anal. Calcd for C₁₁H₁₅Cl: C, 72.32; H, 8.28. Found: C, 72.49; H, 8.41.

2-Azido-2-methyl-4-phenylbutane (8). 2-Chloro-2-methyl-4-phenylbutane (72.0 g, 394 mmol) in *N,N*-dimethylformamide (190 ml) was added slowly (1 hr) to a mixture of sodium azide (50 g, 780 mmol) in DMF (250 ml) at 90°. The mixture was stirred and maintained at 90° for 24 hr and cooled, water (500 ml) was added, and the resulting mixture was extracted with light petroleum (2 × 1 l.) The combined light petroleum extracts were extracted with water (2 × 500 ml), dried, and concentrated to give a light yellow oil (53 g). The oil was chromatographed on alumina (800 g). Elution with light petroleum (1.8 l.) gave a colorless liquid (31.5 g) which contained two components (glc). Repeated chromatography on alumina or preparative glc gave 2-methyl-4-phenyl-2-butene (**26**): bp 108–110° (55 mm) (lit.[41] bp 95° (18 mm)); n²²D 1.5154 (lit.[41] n¹⁹D 1.5158); ms (70 eV) *m/e* 146 (M⁺). Elution with light petroleum–benzene (20:1, v/v) gave a colorless liquid (8.6 g) which exhibited strong absorption at 2100 cm⁻¹. This liquid was chromatographed again on alumina (400 g) as described above to give a colorless liquid (4.8 g) which was distilled under vacuum to give the azide (**8**) (4.4 g, 6%): bp 55–57° (20 μ); ir (liquid film) 2100 (N₃ asym. str.) and 1260 cm⁻¹ (N₃ sym. str.); uv (C₆H₁₂) λ_max sh 281 nm (ε 42) and 266, 262, 258, and 256 (ε₂₅₈ 233); nmr (CCl₄) τ 2.93 (m, 5), 7.42 (m, 2), 8.31 (m, 2), and 8.75 (s, 6).

Anal. Calcd for C₁₁H₁₅N₃: C, 69.81; H, 7.99. Found: C, 69.91; H, 8.08.

2-Amino-2-methyl-4-phenylbutane (29). Sulfuric acid (10 g, 100 g, 100 mmol) in acetic acid (12 ml) was added portionwise to a mixture of 2-methyl-4-phenyl-2-butanol (7.90 g, 48 mmol), sodium cyanide (2.4 g, 48 mmol), and acetic acid (12 ml), with vigorous stirring. The resulting mixture was heated at 75° for 0.5 hr, cooled, and stirred at room temperature for 2 hr. The mixture was poured

into water (250 ml); the aqueous layer was neutralized (solid Na₂CO₃) and extracted with ether (2 × 100 ml). The combined extracts were dried (MgSO₄) and concentrated to give a yellow oil (8.7 g), which was mixed with 20% aqueous sodium hydroxide (85 ml) and boiled under reflux for 12 hr. The mixture was extracted with ether (2 × 50 ml); the combined extracts were dried and concentrated to give a yellow oil (6.1 g), which was dissolved in benzene (100 ml). Hydrogen chloride gas was passed into the benzene solution and the white precipitate which formed was filtered and washed with benzene. It was dissolved in hot ethanol (50 ml) and treated with activated charcoal, and the solution was concentrated to 20 ml and cooled to give the amine hydrochloride (4.0 g), mp >360°.

Anal. Calcd for C₁₁H₁₈ClN: C, 66.15; H, 9.08. Found: C, 65.92; H, 8.76.

The free base was liberated with 6 *M* aqueous NaOH and extracted with ether to give the amine **29** (2.2 g, 28%): bp 128–130° (45 mm); ir (liquid film) 3350 and 3270 cm⁻¹ (NH₂ asym. and sym. str.); nmr (CCl₄) τ 2.95 (m,5), 7.44 (m, 2), 8.47 (m, 2), 8.94 (s, 6), and 9.12 (s, 2, collapses on addition of D₂O).

2-Methyl-4-phenylbutane (27). This was isolated by preparative glc from the products of thermolysis of azide **8** as a colorless liquid: n¹⁹D 1.4885 (lit.[42] n²⁰D 1.4860); ir (film) 1380 and 1360 cm⁻¹ (*gem*-dimethyl); nmr (CCl₄) τ 2.89 (m, 5), 7.40 (m, 2), 8.44 (m, 3), and 9.02 (d, J = 6 Hz); ms (70 eV) *m/e* 148 (M⁺).

2-Biphenylyldiphenylmethane (15), obtained from the thermolysis mixture from azide **5** by preparative glc, had mp 139–141° (lit.[9] mp 138°); ms (70 eV) *m/e* 320 (M⁺).

Thermal Decompositions. All thermolyses were carried out in a Pyrex tube [1.7 cm o.d. × 14 cm] connected to a condenser leading to a mercury trap. The glassware for all decompositions was dried at 160° for 8 hr, cooled in a desiccator, and flushed with dry nitrogen. The Pyrex tube containing the azide was placed in a Woods metal bath which had been brought to the desired temperature. The volume of gas evolved was monitored. A number of glc columns were used to analyze the azide decomposition products: column 1, 6 ft × 0.175 in., packed with SE-30 (20%) on Chromosorb W (60–100 mesh); column 2, 5 ft × 0.25 in., packed with SE-30 (3%) on Varaport 30 (100–120 mesh); column 3, 5 ft × 0.25 in., packed with SE-52 (10%) on Chromosorb W (60–100 mesh); column 4, 6 ft × 0.175 in., packed with SE-30 (gc grade) (20%) on Gas Chrom Q (60–100 mesh). Table IV summarizes the pertinent

Table IV. Conditions for Quantitative Analysis of the Azide Thermolysis Mixtures[a]

Azide	Glc column	Internal standard	Temp
4	1	Diphenyl ether	190° (17 min) followed by 190–240° at 40°/min
5	1	Diphenyl ether	100–200° at 8°/min
	2	Triphenylmethane	150–250° at 4°/min
6	1	Naphthalene	100–144° at 2°/min
7	3	Diphenyl ether	140–240° at 4°/min
8	4	Benzophenone	100–174° at 2°/min followed by 174–260° at 10°/min

[a] Accuracy (from analyses of various mixtures) was about ±3% of the value determined when the amount of the component was in the range of 15–100%, but was lower for the lower percentage components. Reproducibility between injections was ±1% of the value being determined, and reproducibility between decompositions was usually ±5% of the value being determined.

data concerning the quantitative analyses of the azide thermolysis mixtures. Only one typical decomposition is illustrated below. The yields given in the schemes in the Results are the averages of at least two, and up to five, runs.

Thermolysis of 2-(2'-Biphenyl)isopropyl Azide (4). The azide (138.0 mg, 0.582 mmol) was heated in the absence of solvent at 185–190° for 13 hr in the thermolysis apparatus (*vide supra*). Diphenyl ether (41.8 mg, 0.246 mmol) was added and the mixture was dissolved in benzene (30 ml). The solution was boiled under reflux with 3 *N* hydrochloric acid (15 ml) for 24 hr, and the aqueous layer

(40) P. Warrick, Jr., and W. H. Saunders, Jr., *J. Amer. Chem. Soc.,* **84,** 4095 (1962).

(41) A. J. Birch, *J. Chem. Soc.,* 809 (1945).

(42) H. Pines and V. Mark, *J. Amer. Chem. Soc.,* **78,** 4316 (1956).

was basified (6 N NaOH). The layers were separated and the aqueous portion was extracted with benzene (2 × 30 ml). The combined extracts were dried (MgSO₄), concentrated to 10 ml by distillation of the solvent through a 10-cm Vigreux column, and analyzed on column 1 (Table IV). The yields given in Scheme 1 are the average of five such runs.

Reaction of Azide (8) and *N*-Isopropylidene-2-phenethylamine (30). A mixture of **8** (67.2 mg, 0.356 mmol) and the imine **30**[8] (52.7 mg, 0.327 mmol) was heated in the thermolysis apparatus at 180° for 2.0 hr. Benzophenone (72.7 mg, 0.400 mmol) in benzene (1.0 ml) was added and the solution was analyzed on column 4. Table 1 summarized the results, and those of similar runs at 146 and 162°.

Reaction of *N*-Isopropylideneaniline (19) with *N*-(α-Methylbenzylidene)methylamine (20). Imine **19**[8] (9.4 mg, 0.071 mmol) and **20**[8] (9.4 mg, 0.071 mmol) were heated in the thermolysis apparatus for 10 hr at 190–195°. The brown residue was dissolved in benzene (0.2 ml) and analyzed on column 1. The mixture was found to consist of aniline, acetophenone, and *N*-(α-methylbenzylidene)aniline (**22**)[10] in an area ratio of 17:13:70, respectively. There was no indication of a trace of either starting imine or of any other component in the gas chromatogram.

Mass Spectra of Imines. These were determined using an ionization potential of 70 eV, an accelerating voltage of 1.2 kV, and a source temperature of 250°.

N-Isopropylidene-2-aminobiphenyl (**11**): 209 (M⁺, 28), 207 (4), 195 (17), 194 (100), 193 (4), 153 (10), 152 (32), 151 (8), 127 (4), 97 (11), 77 (4), 76 (15), 63 (5), 51 (5), 44 (7), and 39 (6).

N-[α-(2-Biphenylyl)ethylidene]methylamine (**12**):[8] 209 (M⁺, 19), 208 (100), 195 (4), 194 (26), 193 (5), 179 (9), 178 (7), 165 (10), 152 (11), 151 (5), 97 (4), 76 (4), 56 (22), and 44 (5).

N-Benzhydrylidene-2-aminobiphenyl (**16**): 333 (M⁺, 44), 332 (17), 257 (22), 256 (100), 254 (8), 182 (7), 178 (30), 169 (11), 168 (9), 167 (14), 166 (25), 165 (31), 153 (12), 152 (55), 151 (19), 105 (17), 77 (21), and 51 (12).

2-Phenylbenzophenone anil (**17**): 333 (M⁺, 37), 332 (100), 256 (13), 254 (5), 242 (5), 241 (22), 180 (17), 178 (8), 152 (9), 151 (5), 77 (54), and 51 (21).

N-Isopropylideneaniline (**19**):[8] 133 (M⁺, 43), 118 (100), 77 (78), 59 (9), 51 (23), and 39 (9).

N-(α-Methylbenzylidene)methylamine (**20**):[8] 133 (M⁺, 31), 132 (12), 119 (9), 118 (100), 105 (7), 103 (7), 91 (12), 77 (34), 56 (29), 51 (13), and 50 (5).

N-(α-Methylbenzylidene)aniline (**22**): 195 (M⁺, 34), 180 (77), 118 (15), 78 (10), 77 (100), 51 (49), and 39 (10).

N-(6-Undecylidene)-1-pentylamine (**24**): 239 (M⁺, 3), 238 (2), 210 (12), 196 (25), 183 (12), 182 (8), 168 (22), 154 (8), 141 (8), 140 (35), 128 (5), 127 (36), 126 (23), 114 (6), 113 (7), 112 (66), 99 (11), 98 (53), 85 (5), 84 (8), 72 (7), 71 (90), 70 (12), 69 (8), 58 (26), 57 (9), 56 (9), 55 (27), 54 (6), 44 (7), 43 (100), 42 (8), 41 (44), and 39 (8).

N-[2-(4-Phenyl)butylidene]methylamine (**28**):[8] 161 (M⁺, 38), 160 (13), 146 (25), 105 (15), 91 (19), 84 (15), 77 (6), 70 (11), 65 (8), 57 (14), 56 (100), 51 (6), 42 (18), 41 (6), and 39 (7).

N-Isopropylidene-2-phenethylamine (**30**): 161 (M⁺, 6), 146 (7), 105 (12), 91 (6), 77 (5), 71 (5), 70 (100), 56 (9), 42 (5), 41 (5), and 39 (3).

Mass Spectra of Azides. Triphenylmethyl azide: 257 (M − N₂, 1), 256 (2), 254 (1), 244 (9), 243 (100), 180 (24), 166 (7), 165 (52), 77 (63), and 51 (52).

2-Biphenylyldiphenylmethyl azide (**5**): 333 (M − N₂, 5), 332 (11), 320 (12), 319 (37), 318 (57), 317 (26), 256 (11), 242 (37), 241 (100), 240 (11), 239 (27), 178 (5), 165 (23), 159 (9), 152 (10), 151 (10), 145 (5), 77 (19), 51 (9), and 43 (16).

α-Methylbenzyl azide: 147 (M⁺, 5), 119 (13), 118 (7), 106 (10), 105 (100), 104 (50), 103 (17), 91 (5), 79 (12), 78 (22), 77 (70), 76 (7), 63 (7), 52 (12), 51 (39), 50 (20), 43 (14), and 39 (13).

2-Phenylisopropyl azide (**6**): 161 (M⁺, 0.5), 133 (3), 120 (10), 119 (100), 118 (76), 117 (45), 116 (6), 115 (14), 104 (6), 103 (40), 102 (7), 92 (6), 91 (40), 79 (9), 78 (29), 77 (67), 76 (8), 75 (5), 74 (5), 65 (9), 63 (9), 58 (7), 56 (8), 52 (7), 51 (39), 50 (16), 43 (13), 41 (21), and 39 (21).

2-(4′-Biphenylyl)isopropyl azide:[43] 237 (M⁺, 5), 209 (5), 196 (15), 195 (97), 194 (100), 193 (6), 180 (10), 179 (42), 178 (32), 177 (7), 176 (6), 167 (16), 165 (5), 164 (11), 155 (8), 154 (13), 153 (18), 152 (30), 151 (13), 150 (7), 97 (7), 91 (5), 89 (9), 88 (5), 84 (5), 83 (5), 82 (5), 77 (13), 76 (15), 75 (10), 74 (6), 63 (10), 62 (5), 57 (5), 56 (7), 55 (5), 52 (5), 51 (13), 50 (7), 43 (23), 41 (15), 40 (12), and 39 (11).

2-(2′-Biphenylyl)isopropyl azide (**4**): 209 (M − N₂, 1), 208 (2), 195 (14), 194 (67), 193 (9), 180 (17), 179 (100), 178 (47), 177 (10), 176 (9), 167 (5), 165 (13), 153 (6), 152 (18), 151 (9), 115 (5), 89 (16), 88 (7), 77 (6), 76 (12), 75 (6), 74 (5), 63 (9), 51 (11), 50 (6), 43 (18), and 39 (8).

2-Azido-2,3,3-trimethylbutane:[43] 113 (M − N₂, 0.2), 99 (10), 98 (2), 83 (4), 58 (9), 57 (100), 56 (40), 55 (7), 43 (25), 42 (15), 41 (42), and 39 (13).

4-Azidoheptane:[43] 113 (M − N₂, 0.3), 112 (0.4), 99 (1), 98 (4), 85 (4), 84 (4), 70 (22), 57 (34), 56 (10), 55 (6), 44 (5), 43 (100), 42 (12), 41 (41), and 39 (9).

Tri-*n*-pentylmethyl azide (**7**): 239 (M − N₂, 0.05), 238 (0.1), 255 (2), 210 (0.5), 196 (1), 170 (1), 169 (1), 168 (4), 99 (10), 98 (100), 85 (9), 71 (28), 70 (4), 69 (8), 57 (24), 56 (10), 55 (21), 43 (99), 42 (9), 41 (34), and 39 (6).

2-Azido-2-methyl-4-phenylbutane (**8**): 161 (M − N₂, 3), 160 (9), 146 (11), 131 (19), 106 (12), 105 (20), 104 (29), 103 (7), 92 (8), 91 (100), 79 (7), 78 (7), 77 (14), 70 (5), 65 (15), 63 (6), 56 (35), 51 (14), 50 (6), 43 (5), 42 (9), 41 (15), and 39 (18).

(43) The synthesis and other properties of these compounds will be described elsewhere.