removed and added to weighed quantities of individual authentic isomers in separate flasks. Wasteful recrystallizations and chromatography on alumina, along with the use of the "hold-back carrier" technique[31] finally gave pure samples for carbon-14 assay.

A typical run involved the use of 400–500 mg. of triphenylcarbinol-C^{14} and 30 ml. of solvent. A 1- to 2-g. sample of authentic isomer usually was employed for the dilution procedure.[32] Carbon-14 assays[31] were made on samples of purified isomer that weighed 10–15 mg.

(32) Details concerned with the scintillation counting technique and the use of a simplified counting chamber may be obtained from the Ph.D. Thesis of W. Schroeder, Purdue University, 1958.

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LAFAYETTE, IND.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Free Radical Additions of Amines to Olefins[1]

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The free radical, chain additions of amines to olefins in the presence of peroxides or light give higher homologous amines which are products of α-C-alkylation. For example, the reaction of piperidine with propene gives *d,l*-coniine (2-propylpiperidine), and the reactions of pyrrolidine or piperidine with allyl alcohol yield 2-(3-hydroxypropyl)-pyrrolidine or 2-(3-hydroxypropyl)-piperidine which can be converted to pyrrolizidine (1-azabicyclo[3.3.0]octane) or *d,l*-δ-coniceine (1-azabicyclo[4.3.0]nonane), respectively. Interesting specificities are observed: (1) apparently intermediate free radicals abstract only the α-hydrogen atoms of the amines, and (2) alkyl peroxides or light are effective inducing agents while benzoyl peroxide is not. Relative yields decreasing in the order—secondary azacyclanes, primary alkylamines, tertiary azacyclanes, secondary and tertiary alkylamines—suggest steric and statistical influences.

The novel reactions of amines with olefins reported here provide a useful synthetic tool in the preparation of more complex amines, alkaloids and alkaloid intermediates. In common with other free radical additions, terminal olefins give higher yields than non-terminal ones. The utility of the reaction is extended since olefins with other functional groups (hydroxyl and cyano, which do not react with amines under the reaction conditions) may be used.

The reactions of amines with olefins studied and the 1:1 products obtained are summarized in Table I. Some of these products were identified by the comparison of their physical properties, derivatives and infrared spectra with those of the known amines prepared by other means: (1) 4-aminododecane and 6-aminotetradecane prepared by the reaction of formic acid and ammonium formate with dodecanone-4 and tetradecanone-6, respectively; (2) 2-hexylpiperidine and 2-octylpiperidine prepared by the reduction of the 2-alkylpyridines formed from α-picoline with *n*-amyl or *n*-heptyl bromides and sodamide; and (3) 2-octyl-N-methylpiperidine prepared from the above 2-octylpiperidine by its reaction with formaldehyde and formic acid. The physical properties of the 2-ethylpiperidine, 2-propylpiperidine and 2-(3-hydroxypropyl)-piperidine were those observed in previous work. The 2-(3-hydroxypropyl)-pyrrolidine and 2-(3-hydroxypropyl)-piperidine were further identified by their conversion to pyrrolizidine and δ-coniceine, respectively.

In all of the experiments listed higher boiling products (higher telomers) were obtained but were not identified. Details are given in Table II. The following reactions were attempted (with *t*-butyl peroxide at 120–130°), but addition products were obtained in amounts too small for separation and identification[2]: (1) diethylamine with 1-octene, (2) triethylamine with 1-octene, (3) dibutylamine with 1-octene, (4) dibutylamine with allyl alcohol, (5) tributylamine with 1-octene, and (6) N,N-dimethylcyclohexylamine with 1-octene. No addition products were obtained when a mixture containing piperidine, 1-octene and benzoyl peroxide was heated at 100° for 15 hours.

TABLE I

PRODUCTS IN THE ADDITIONS OF AMINES TO OLEFINS[a]

Amine	Olefin	Products
Butylamine[b]	1-Octene	4-Aminododecane[d]
Hexylamine	1-Octene	6-Aminotetradecane[d]
2-Aminopropane	1-Octene	2-Amino-2-methyldecane[e]
Cyclohexylamine	1-Octene	1-Amino-1-octylcyclohexane[e]
Pyrrolidine	Allyl alcohol	2-(3 Hydroxypropyl)-pyrrolidine[d]
Piperidine	Ethene	2-Ethylpiperidine[d]
Piperidine	Propene	2-Propylpiperidine[d]
Piperidine	1 Hexene	2-Hexylpiperidine[d]
Piperidine[b]	1 Octene	2-Octylpiperidine[d]
Piperidine[c]	Allyl alcohol	2-(3-Hydroxypropyl)-piperidine[d]
Piperidine	Allyl cyanide	2-(3-Cyanopropyl)-piperidine[e]
γ-Pipecoline	Allyl alcohol	2-(3-Hydroxypropyl)-4-methylpiperidine[e]
N-Methylpiperidine	1-Octene	2-Octyl-N-methylpiperidine[d]

[a] All reactions were obtained with *t*-butyl peroxide. [b] Induced by *t*-butyl peroxide and light. [c] Induced by *t*-butyl peroxide, *t*-amyl peroxide and 2,2-bis-(*t*-butylperoxy)-butane. [d] Structure proved. [e] Structure assumed.

Discussion

A free radical, chain reaction of short chain length is suggested by the experimental observations: (1) the reactions are induced by light quanta or alkyl peroxides in such amounts as to indicate that a single initiation of reaction leads to the for-

(1) Previous communication, W. H. Urry, O. O. Juveland and F. W. Stacey, THIS JOURNAL, 74, 6155 (1952).

(2) O. O. Juveland, Ph.D. Dissertation, University of Chicago, 1953.

TABLE II

	Amine (moles)	Olefin (mole)	Initiator, mole	T, °C.	Olefin used (mole)	Conversion to telomers,[a] % 1:1	2:1	Residue (Tel)[b]
1	Butylamine (5.06)	1-Octene (0.25)	0.031[g]	123–126	0.111	36	18	46(3.0)
2	Butylamine (6.7)	1-Octene (0.26)	[h]	30–35		0.001[d]		6.35[e]
3	Hexylamine (4.53)	1-Octene (0.23)	.031[g]	124–127	.21	36	17	47(3.5)
4	2-Aminopropane (2.0)	1-Octene (0.16)	.031[g]	118–122	.152	46	14.6	39.4(2.37)
5	Cyclohexylamine (5.00)	1-Octene (0.223)	.041[g]	124–128	.198	55	14	31(2.4)
6	Pyrrolidine (5.34)	Allyl alcohol (0.40)	.034[g]	120–122	.343	63		37(3.3)
7	Piperidine (0.95)	Ethene[f]	.028	125		0.023[d]		1.1[e]
8	Piperidine (1.03)	Propene[f]	.02[g]	125		0.032[d]		2.6[e]
9	Piperidine (4.23)	1-Hexene (0.273)	.034[g]	122	.154	60	15	25(2.9)
10	Piperidine (4.50)	1-Octene (0.36)	.048[g]	120	.231	70	16	14(3.24)
11	Piperidine (2.44)	1-Octene (0.183)	[h]	30–55		0.005[d]		
12	Piperidine (4.52)	Allyl alcohol (0.327)	.031[g]	122–130	.282	54		46(3.4)
13	Piperidine (4.00)	Allyl alcohol (0.328)	.035[c]	100		0.03[d]		4.2[e]
14	Piperidine (2.11)	Allyl alcohol (0.155)	.0064[i]	95		0.07[d]		26[e]
15	Piperidine (4.39)	Allyl cyanide (0.313)	.034[g]	120–124	.286	48	24	28(3.4)
16	γ-Pipecoline (2.0)	Allyl alcohol (0.17)	.02[g]	123–125	.14	42		58(2.52)
17	N-Methylpiperidine (2.5)	1-Octene (0.18)	.041[g]	122–126	.13	22	32	46(3.0)

[a] Percentage conversion to each telomer based upon olefin consumed. [b] Average number of olefin units per molecule of residue. [c] *t*-Amyl peroxide induced. [d] Conversion to products given in moles. [e] Residue yield in grams. [f] Pressure of propene or ethene, 30–40 p.s.i. [g] *t*-Butyl peroxide induced. [h] Ultraviolet light induced. [i] 2,2-Bis-(*t*-butylperoxy)-butane induced.

mation of significantly more than one molecule of product, and (2) telomeric products, hitherto shown to be characteristic of this kind of reaction, are obtained. The reaction of piperidine with ethylene may be used to illustrate

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \quad (1)$$

$$(CH_3)_3CO\cdot + \text{piperidine} \longrightarrow (CH_3)_3COH + \text{I} \quad (2)$$

$$\text{piperidine} + CH_2{=}CH_2 \longrightarrow \text{II} \quad (3)$$

$$\text{II} + \text{piperidine} \longrightarrow \text{piperidine} + \text{I} \quad (4)$$

$$\text{II} + CH_2{=}CH_2 \longrightarrow \text{III} \quad (5)$$

$$\text{III} + \text{piperidine} \longrightarrow \text{piperidine} + \text{I} \quad (6)$$

$$2\,\text{piperidyl} \longrightarrow \text{piperidine} + \text{dehydropiperidine} \quad (7)$$

Reactions 1 and 2 initiate the chain (*t*-butyl alcohol is the principal peroxide-derived product in these reactions; no acetone or methane was isolated), and 3 and 4 are chain-propagating steps to form the 1:1 product. Reactions 3, 5 and 6 are a chain sequence to the 2:1 product. The reactions of chain transfer (4) and chain growth (5) compete. A high ratio of amine to olefin in the reaction mixture favors the former. However, the relative rates of reactions 4 and 5 depend also upon the amine and the olefin used. For example, with comparable molar ratios of amines to olefins, piperidine reacts to give relatively good yields (50–70%) of the 1:1 telomers while primary amines such as butylamine and hexylamine give lower yields (35%). Further, under comparable conditions piperidine adds to various olefins to give different yields of the 1:1 telomers: with 1-octene, 70%; with 1-hexene, 60%; with allyl alcohol, 54%; and with allyl cyanide, 48%. A more quantitative illustration of these effects is apparent from the transfer constants calculated for the reactions studied and listed in Table III.

TABLE III

TRANSFER CONSTANTS[3] FOR AMINE–OLEFIN ADDITION REACTIONS

	Amine	Olefin	[M]/[S]	$\bar{P}$	C
1[a]	Butylamine	1-Octene	0.039	1.63	0.062
3	Hexylamine	1-Octene	.049	1.69	.070
4	2-Aminopropane	1-Octene	.043	1.45	.095
5	Cyclohexylamine	1-Octene	.025	1.31	.081
6	Pyrrolidine	Allyl alcohol	.044	1.35	.126
9	Piperidine	1-Hexene	.048	1.34	.141
10	Piperidine	1-Octene	.057	1.21	.259
12	Piperidine	Allyl alcohol	.042	1.48	.088
15	Piperidine	Allyl cyanide	.040	1.45	.089
16	γ-Pipecoline	Allyl alcohol	.051	1.54	.094
17	N-Methylpiperidine	1-Octene	.047	1.88	.053

[a] Numbers correspond to those of the experiments listed in Table II which provided the data for the calculations.

(3) Transfer constants have been calculated according to the equation of Mayo (F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943); R. A. Gregg and F. R. Mayo, *Disc. Faraday Soc.*, **2**, 328 (1947): *viz.*, $\bar{P} = [M]/C[S] + 1$ where $\bar{P}$ is the average number of olefin units per molecule of product, [M]/[S] is the average molar ratio of olefin to amine and C is the transfer constant (the ratio of rate constant for chain transfer, 4, over that for chain growth, 5).

The values calculated for the transfer constants are not reliable because of the low average molecular weights of the products, but they indicate semi-quantitatively the relative ease of chain transfer in the amine–olefin reactions studied. The transfer constants shown are higher than those obtained in alcohol–olefin additions (secondary alcohols such as propanol-2 and butanol-2, 0.052 to 0.063; primary alcohols such as ethanol and butanol-1, 0.017 to 0.027[4]). Amines, therefore, undergo the chain transfer reaction with greater ease than alcohols.

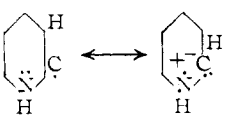
All of the primary amines studied (butylamine, hexylamine, 2-aminopropane and cyclohexylamine) gave with 1-octene satisfactory yields of addition products with the expected higher transfer constants with those amines in which a tertiary hydrogen atom is transferred (2-aminopropane and cyclohexylamine). With the secondary amines, only the heterocycles (piperidine, γ-pipecoline and pyrrolidine) gave good yields, while others such as diethylamine and dibutylamine gave low yields. The only tertiary amine to give a successful addition reaction was N-methylpiperidine while triethylamine and tributylamine were unreactive.

These results may be attributed to steric and statistical effects. The lack of reactivity of dialkyl- and trialkylamines suggests difficulty of access to the α-hydrogen atoms unless a ring structure holds those atoms in favorable alignment. The low transfer constant with N-methylpiperidine may also be a steric effect. The fact that the heterocycles (piperidine and pyrrolidine) are more reactive (higher transfer constants) than the primary amines may be due to the greater number of transferable hydrogen atoms in the former (four *versus* one or two).

Discussion of chain termination reactions is dominated by the experimental facts that, in these reactions of amines with the higher 1-alkenes, the 1:1 products were obtained in high purity by simple distillation: (1) their infrared spectra were identical in detail with those of the same amines prepared by alternate syntheses, (2) tests for unsaturation revealed none (no hydrogen absorbed with attempted hydrogenation over Adams catalyst; similar tests showed that 2:1 products were saturated), and (3) their derivatives were obtained in high yield and required little purification. These observations are remarkable since relatively large amounts of initiator (*t*-butyl peroxide or light) were necessary to accomplish these additions and, as a consequence, relatively large amounts of products of chain termination reactions are to be expected. Such possible products include those from disproportionation or dimerization of radicals such as I, II or III; or from dimerization of allylic radicals obtained via abstraction of hydrogen atoms from the α-methylene group of the olefins. It is likely, therefore, that step 7 of the reaction scheme represents the principal chain-breaking reaction since it is the only one likely to give pure 1:1 products with our isolation techniques. In step 7, two chain-carrying radicals are consumed, a molecule of amine is regenerated, and a molecule of aldimine or ketimine is formed (most of the latter probably codistilled with the excess of recovered amine in our experiments). In many of our experiments, however, small fractions of higher refractive index and slightly lower boiling point than the 1:1 products were obtained. As illustrated in the addition of cyclohexylamine to 1-octene (see Experimental part), such forerun fractions contained unsaturates while the main fraction of 1:1 product (here 1-amino-1-octylcyclohexane) was shown to be saturated. Of the possible unsaturated products here (cyclohexanonimine, 1-amino-1-octen-1-ylcyclohexane or their isomers), the former is the most likely component of these fractions since it is unlikely that the latter could have been so separated from the 1-amino-1-octylcyclohexane. Other modes of chain termination would have given mixtures of 1:1 products with dimers from amine-derived radicals (as I) or with unsaturated amines of about the same molecular weight; or would have given much larger amounts of high boiling residue products than were observed (*via* dimerization of the more complex radicals).

It is likely, therefore, that this favorable chain termination is chiefly responsible for the success as a preparative method of these reactions which might otherwise have been rendered useless by their short chain length and the low transfer constants of the amines. Similar considerations apply to the comparable reactions of alcohols with olefins[4] where similar experimental evidence was obtained for the above type of chain termination (1:1 and 2:1 products saturated, and ketone disproportionation products observed).

The fact that free radical attack upon hydrogen attached to the α-carbon atom occurs rather than upon hydrogen attached to nitrogen may seem surprising. The bond energies (H_2N–H, 102 kcal./mole[5]; H_3C–H, 102 kcal./mole)[6] are approximately equal. The mode of attack observed may be due to resonance stabilization, illustrated below for the resulting free radical, of the transition state.



This site of attack is even more surprising in view of the results of Gambarjan[7] in which the reactions of benzoyl peroxide with secondary amines gave O-benzoylhydroxylamines and benzoic acid (see later discussion).

As in alcohol–olefin reactions, the additions of amines to olefins are induced by light or alkyl peroxides (*t*-butyl peroxide, *t*-amyl peroxide or 2,2-bis-*t*-butylperoxybutane), but benzoyl peroxide is ineffective. This difference between the peroxides previously was attributed to induced decomposition of benzoyl peroxide with ethers and alcohols. This reaction has been shown to be a free-radical chain reaction in which the chain-propagating steps are: (1) attack by a free benzoate radical to give benzoic acid and a free radical derived from

(4) W. H. Urry, F. W. Stacey, E. S. Huyser and O. O. Juveland, THIS JOURNAL, **76**, 450 (1954).

(5) M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

(6) D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).

(7) S. Gambarjan, *Ber.*, **42**, 4003 (1910); **58B**, 1775 (1925); **60B**, 390 (1927).

the alcohol or ether, and (2) attack by the latter free radical upon benzoyl peroxide to give acylals from ethers, or hemiacylals from alcohols, and another free benzoate radical.[8-10]

Benzoyl peroxide reacts rapidly with amines (explosions occur if the temperature is not carefully controlled). Its failure to induce amine–olefin reactions may be due in part to free-radical, chain reactions with amines analogous to those described above. Further, the greater basicities of amines permit ionic reactions of two types with benzoyl peroxide. Recent extensive investigations by Horner and his co-workers[11,12] have shown that one such reaction path probably gives initially quaternary hydroxylamine derivatives ($R_3NOOCC_6H_5^+$ $C_6H_5COO^-$); and in a second (observed with aniline), ammonolysis occurs to give benzanilide and perbenzoic acid which reacts further. Some reaction products obtained may be assumed to be formed by subsequent proton-transfer reactions of the quaternary hydroxylammonium ions with bases present (amine or benzoate ion) to give products directly (O-benzoylhydroxylamines from secondary amines) or to give intermediates which rearrange to give products (α-benzoyloxyamines from tertiary amines). Other products may result from free radical decomposition of the positive ion (tertiary amine–benzoyl peroxide reaction mixtures absorb nitric oxide and oxygen, and also initiate polymerization).

The work reported here, however, implies that one amine–acyl peroxide interaction may be a free-radical, chain reaction of the type postulated for ethers and alcohols. Some existing evidence suggests this possibility: (1) marked variation of reaction rate is observed in different solvents, (2) styrene decreases the rate in "fast" solvents[12] and (3) oxygen absorption by tertiary amine–benzoyl peroxide reaction mixtures continues for a longer time than that observed for the peroxide reaction in the absence of oxygen[11] to suggest that the latter may inhibit. The free-radical chain mechanism would be expected to be most important in the reactions of tertiary alkyl amines, (to give α-benzoyloxyamines) in less polar solvents and at higher temperatures.

Experimental Part

Reagents.—Piperidine (Eastman white label, b.p. 105–106°, $n^{20}D$ 1.4529), butylamine (Eastman, b.p. 77–78°, $n^{20}D$ 1.4013), hexylamine (Matheson, b.p. 128–129°, $n^{20}D$ 1.4192), cyclohexylamine (Eastman, b.p. 134–134.5°, $n^{20}D$ 1.4595) and pyrrolidine (Matheson, Coleman and Bell, b.p. 87.5–88.5°, $n^{20}D$ 1.4433) were distilled through a 12-plate Fenske column immediately before they were used. Allyl alcohol (Shell, b.p. 96–97°, $n^{20}D$ 1.4138), allyl cyanide (Eastman, b.p. 118–119°, $n^{20}D$ 1.4073), 1-hexene (Phillips, b.p. 83.8°, $n^{20}D$ 1.3875), 1-octene (Humphrey–Wilkinson, b.p. 120–121°, $n^{20}D$ 1.4090) and *t*-butyl peroxide (Shell, b.p. 49.5° at 77 mm., $n^{20}D$ 1.3893) were distilled in the same way. Ethene (Matheson C.P.) and propene (Matheson C.P.) were used without purification.

N-Methylpiperidine (b.p. 105–106°, $n^{20}D$ 1.4387) was prepared by the reaction (Leuckart) of piperidine with formaldehyde and formic acid.[13] *t*-Amyl peroxide (b.p. 46° at 13 mm., $n^{20}D$ 1.4095) was prepared by the method of Milas and Surgenor.[14] 2,2-Bis-(*t*-butylperoxy)-butane (b.p. 50° at 2 mm., $n^{20}D$ 1.4145) was prepared by the reaction of *t*-butyl hydroperoxide with butanone-2 in the presence of concentrated sulfuric acid.[15]

Apparatus.—The use of *t*-butyl peroxide (half-life in tri-*n*-butylamine at 125°, 11.3 hours; and at 135°, 4.6 hours) required reaction temperatures between 120 and 130°. Reactions between higher boiling substances were performed in three-necked, round-bottomed flasks equipped through ground glass joints with a dropping funnel, a thermometer well and a reflux condenser, the outlet of which was attached to a mercury bubbler. If the boiling temperature of the reaction mixture at atmospheric pressure was below 120°, the reaction was carried out in a glass bomb tube placed in an electrically-heated cylindrical oil-bath. Some reactions with piperidine were run in a special all-glass apparatus, a 1-liter, round-bottomed flask with a condenser and a dropping funnel fused to it so that the system could be kept under nitrogen pressure.

The Addition of Butylamine to 1-Octene.—A reaction mixture containing butylamine (370 g., 5.07 moles), 1-octene (28 g., 0.25 mole) and *t*-butyl peroxide (4.5 g., 0.031 mole) in a glass bomb tube was heated at 123–126° for 48 hours, It was then distilled through a 12-plate Fenske column to give *t*-butyl alcohol (2.5 g.), unreacted 1-octene (12.35 g., 0.11 mole) and butylamine. The residual addition products were distilled through a Vigreux column to give 4-aminododecane (7.35 g., b.p. 70–71° at 1 mm., $n^{20}D$ 1.4407).

Anal. Calcd. for $C_{12}H_{27}N$: C, 77.76; H, 14.68; N, 7.56; mol. wt., 185.3. Found: C, 78.20; H, 14.50; N, 7.42; mol. wt., 192.

This product was identified by a comparison of its chemical and physical properties with 4-aminododecane (b.p. 69–71° at 1 mm., $n^{20}D$ 1.4408) prepared (34% yield) by the reaction of formic acid and ammonium formate[16] with dodecanone-4 (prepared, 59% yield, by the benzoyl peroxide-induced reaction of *n*-butyraldehyde with 1-octene).[17] Reaction of this addition product with phenyl isothiocyanate gave its phenylthiourea derivative (m.p. 58–58.5°, m.p. of mixture with the authentic sample 58–58.5°).

Anal. Calcd. for $C_{19}H_{32}N_2S$: N, 8.74. Found: N, 8.81.

Its hydrochloride (m.p. 88.5–90°, m.p. of mixture with authentic sample 88–90°) also was prepared. *Anal.* Calcd. for $C_{12}H_{28}NCl$: N, 6.31. Found: N, 6.04.

Further distillation of the product gave a fraction (b.p. 110–160°) at 1 mm., $n^{20}D$ 1.4728, 3.0 g., mol. wt. 274). A residue (7.1 g., mol. wt. 406) remained.

4-Aminododecane (1.7 g.) was obtained in small yield when a solution containing butylamine (490 g., 6.7 moles) and 1-octene (30 g., 0.26 mole) was illuminated internally for 120 hours with a quartz mercury resonance lamp (temperature, 30–35°). A higher boiling residue (6.35 g.) also was obtained.

The Addition of Hexylamine to 1-Octene.—A solution of 1-octene (26 g., 0.23 mole) and *t*-butyl peroxide (4.5 g., 0.031 mole) in hexylamine (458 g., 4.53 moles) was held at 124–127° in a 1-liter flask equipped as previously described for 60 hours. Distillation of the reaction mixture gave *t*-butyl alcohol (4 g.), unreacted hexylamine and an addition product shown to be 6-aminotetradecane (16.0 g., b.p. 84–85° at 1 mm., $n^{20}D$ 1.4435).

Anal. Calcd. for $C_{14}H_{31}N$: C, 78.79; H, 14.64; N, 6.56; mol. wt., 213. Found: C, 79.02; H, 14.86; N, 6.30; mol. wt., 202.

Its phenylthiourea derivative (1-(4-tetradecyl)-3-phenylthiourea)(m.p. 69–69.5°, m.p. of mixture with authentic

(8) P. D. Bartlett and K. Nozaki, THIS JOURNAL, **68**, 1686 (1949); **69**, 2299 (1947).

(9) W. E. Cass, *ibid.*, **68**, 1976 (1946); **69**, 500 (1947); **72**, 4915 (1950).

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(11) L. Horner and S. Hartmut, *Ann.*, **606**, 47 (1957); L. Horner and H. Junkermann, *ibid.*, **591**, 53 (1955); L. Horner and W. Kirmse, *ibid.*, **567**, 48 (1955), and preceding papers.

(12) Discussed by C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 590.

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(14) N. A. Milas and D. M. Surgenor, *ibid.*, **68**, 643 (1946).

(15) F. H. Dickey, J. H. Raley, F. F. Rust, R. S. Treseder and W. E. Vaughan, *Ind. Eng. Chem.*, **41**, 1673 (1949).

(16) F. S. Crosley and M. L. Moore, *J. Org. Chem.*, **9**, 529 (1944).

(17) M. S. Kharasch, W. H. Urry and B. M. Kuderna, *ibid.*, **14**, 248 (1949).

sample 69–69.5°) was prepared. *Anal.* Calcd. for $C_{21}H_{36}N_2S$: N, 8.04. Found: N, 8.00.

6-Aminotetradecane (b.p. 84–86° at 1 mm., $n^{20}D$ 1.4432) for comparison was prepared (23% yield) by the reaction of formic acid and ammonium formate with 6-tetradecanone[16] (prepared, 43% yield, by the peroxide-induced reaction of hexanal with 1-octene[17]). Further distillation of the reaction product gave a fraction (5.7 g., b.p. 120–155° at 1 mm., $n^{20}D$ 1.4560, mol. wt. 327). A residue (12 g., average mol. wt. 457) remained.

The Addition of 2-Aminopropane to 1-Octene.—A reaction mixture containing 2 aminopropane (118 g., 2.0 moles), 1-octene (18 g., 0.16 mole) and *t*-butyl peroxide (3 g., 0.02 mole) was heated in a glass bomb tube at 118–122° for 55 hours. After the removal of *t*-butyl alcohol and unreacted 2-aminopropane, a substance presumed to be 2-amino-2-methyldecane (12 g., b.p. 47–48° at 1 mm., $n^{20}D$ 1.4333) was obtained.

Anal. Calcd. for $C_{11}H_{25}N$: C, 77.11; H, 14.71; mol. wt., 171. Found: C, 76.84; H, 14.53; mol. wt., 178.

Its hydrochloride (m.p. 116–117°) was prepared. *Anal.* Calcd. for $C_{11}H_{26}NCl$: C, 63.58; H, 12.61. Found: C, 63.84; H, 12.90.

Further distillation gave a fraction (3.5 g., b.p. 80–120° at 1 mm., average mol. wt. 279) and a residue (5.5 g., average mol. wt. 325) remained.

The Addition of Cyclohexylamine to 1-Octene.—Cyclohexylamine (497 g., 5.02 moles), 1-octene (25 g., 0.223 mole) and *t*-butyl peroxide (6.0 g., 0.041 mole) were placed in the described reflux apparatus and the solution was held at 124–128° for 53 hours. The reaction mixture was then distilled through a 12-plate Fenske column and *t*-butyl alcohol (5.5 g.) and unreacted cyclohexylamine (b.p. 62.5–63° at 69 mm.) were obtained. Distillation of the residual reaction product through a Vigreux column gave the following fractions: I, 1.85 g., b.p. 88–89° at 1 mm., $n^{20}D$ 1.4788; II, 2.7 g., b.p. 89–92° at 1 mm., $n^{20}D$ 1.4772; III, 4.0 g., b.p. 92° at 1 mm., $n^{20}D$ 1.4759; and IV, presumed to be 1-amino-1-octylcyclohexane, 23 g., b.p. 95–97° at 1 mm., $n^{20}D$ 1.4657; no hydrogen absorbed with hydrogenation as described below.

Anal. Calcd. for $C_{14}H_{29}N$: C, 79.54; H, 13.83; N, 6.63; mol. wt., 211. Found: C, 79.20; H, 13.70; N, 6.79; mol. wt., 216.

The hydrochloride of fraction IV was prepared (m.p. 107.5–108.5°). *Anal.* Calcd. for $C_{14}H_{30}NCl$: N, 5.65. Found: N, 5.72.

Its reaction with phenyl isothiocyanate gave the phenylthiourea (m.p. 91–91.5°). *Anal.* Calcd. for $C_{21}H_{34}N_2S$: N, 8.09. Found: N, 8.30.

Distillation was continued to give a fraction (4.8 g., b.p. 150–165° at 1 mm., $n^{20}D$ 1.4770, average mol. wt. 287; also saturated—did not absorb hydrogen in hydrogenation test) which was apparently a mixture of 1-amino-1-octylcyclohexane and the addition product formed from 2 molecules of 1-octene and 1 of cyclohexylamine. A residue (9.4 g., average mol. wt. 366) remained in the distilling flask.

Fractions I, II and III above were combined, and attempts to prepare the above derivatives (hydrochloride, phenylthiourea) from this mixture gave oils which did not crystallize. An aliquot (3.2 g.) was hydrogenated (H_2, 343 ml. S.T.P., 0.0153 mole consumed) over Adams catalyst in a quantitative hydrogenation apparatus.[18] After the solvent (ethanol) and a small forefraction had been distilled from this hydrogenation reaction mixture, only 1-amino-1-octylcyclohexane (1 g., b.p. 94–96° at 1 mm., $n^{20}D$ 1.4680; gave the above phenylthiourea, m.p. 90–91°, "mixed m.p." with that above, 90–91°) was obtained. These preliminary fractions probably were mixtures, therefore, of the 1:1 product with the unsaturated product of disproportionation of the 1-aminocyclohexyl radical (cyclohexanonimine, or its isomers; 1.5 g. in the 3.2-g. aliquot). The high refractive index of fraction I suggests that these products might have been even more unsaturated substances produced from the initial ones by further radical attack and disproportionation. Their reduction would give the lower boiling cyclohexylamine (b.p. 134°) which could be separated more easily by distillation. Other possible unsaturated products (bioctenyls and 1-amino-1-octenylcyclohexanes) could not have been so easily separated by simple distillation from the 1-amino-1-octylcyclohexane.

The Addition of Pyrrolidine to Allyl Alcohol.—A solution of allyl alcohol (23 g., 0.40 mole) and *t*-butyl peroxide (5.0 g., 0.034 mole) in pyrrolidine (380 g., 5.35 moles) was heated in a bomb tube at 120–122° for 48 hours. Direct distillation gave, after removal of the remaining reactants and *t*-butyl alcohol, 2-(3-hydroxypropyl)-pyrrolidine (27.8 g., b.p. 80–81° at 1 mm., $n^{20}D$ 1.4870).

Anal. Calcd. for $C_7H_{15}NO$: C, 65.07; H, 11.70; mol. wt., 129. Found: C, 64.75; H, 11.79; mol. wt., 133.

A residue (10.2 g., average mol. wt. 261) remained in the distilling flask.

The structure of the 2-(3-hydroxypropyl)-pyrrolidine was confirmed by its conversion to pyrrolizidine (1-azabicyclo-[3.3.0]octane) by the method of Prelog, Cerkovnikov and Ustricev.[19] A solution containing this amino alcohol (4.25 g., 0.033 mole) and hydrobromic acid (48%, 95 ml.) was heated in a bomb tube at 100° for 12 hours. Water and excess hydrobromic acid was then removed under reduced pressure, and the residual solid was recrystallized from acetone to give 2-(3-bromopropyl)-pyrrolidine hydrobromide (2.5 g., 0.0092 mole, m.p. 102–103°, 28% yield). This substance (2.5 g.) was added over a period of 2.5 hours to a stirred sodium hydroxide solution (0.1 *N*, 2000 ml.) held at 50°. This reaction mixture was allowed to cool, benzenesulfonyl chloride (3 g., to react with remaining secondary amine) was added, and the resulting mixture was allowed to stand (1 hour). It was then steam distilled and the distillate (50 ml.) was extracted three times with ether. The ether solution was dried over anhydrous sodium sulfate. Picric acid (2 g.) was added to this ether solution, and the picrate of pyrrolizidine (1.5 g., m.p. 256.5–258°, 50% yield) was obtained.[20]

The Addition of Piperidine to Ethene.—In a glass pressure apparatus equipped with a condenser and a dropping funnel, piperidine (81 g., 0.95 mole) with added *t*-butyl peroxide (1.1 g.) was held at 125° for 24 hours under a pressure of ethene (30–40 lb./sq. in.). Additional peroxide (1.8 g., total 2.9 g., 0.02 mole) was added 8 hours after the reaction was begun. Distillation of the reaction mixture gave *t*-butyl alcohol (2.7 g.), unreacted piperidine (72 g.) and a fraction shown to be 2-ethylpiperidine (2.6 g., b.p. 73–75° at 52 mm., $n^{20}D$ 1.4544). Its hydrochloride (m.p. 180–181°), picrate (m.p. 130–131°) and chloroplatinate (m.p. 202–204°)[21] were prepared. A residue (1.1 g.) remained in the distilling flask.

The Addition of Piperidine to Propene.—In the pressure apparatus used for the ethene experiment, a solution of *t*-butyl peroxide (1.2 g.) in piperidine (87 g., 1.03 moles) was held at 125° for 12 hours under a pressure of propene 30–40 lb./sq. in.). Additional peroxide (1.8 g.) was added as the reaction progressed (first 6 hours). After distillation of *t*-butyl alcohol and unreacted piperidine, a residue remained. It was distilled through a 6-plate Fenske column, and *d,l*-coniine (4 g., $n^{23}D$ 1.4513, b.p. 93° at 70 mm.) was isolated. This product was identified by its hydrochloride (m.p. 211–212°) and its platinichloride (m.p. 155–157°).[22,23] Two fractions (0.90 g., b.p. 84–100° at 120 mm., $n^{20}D$ 1.4850; and 0.5 g., b.p. 101–105° at 120 mm., $n^{20}D$ 1.4619) which distilled just before the *d,l*-coniine were of high refractive index. Study of such fractions in other experiments suggests that these are unsaturated derivatives of piperidine probably formed by disproportionation of the 2-piperidyl radical to give tetrahydropyridine and then subsequent free radical attack upon it. A residue (2.6 g.) remained.

The Addition of Piperidine to 1-Hexene.—Piperidine (360 g., 4.23 moles), 1-hexene (23 g., 0.274 mole) and *t*-butyl peroxide (5 g., 0.034 mole) were heated in a bomb tube at 122–125° for 50 hours. Distillation of the reaction mixture through a 12-plate fractionating column packed with single-turn glass helices gave *t*-butyl alcohol (3.7 g.), unreacted 1-hexene (8.5 g.) and piperidine. The residual product was distilled to give a product shown to be 2-hexylpiperidine (15.6 g., b.p. 77–78° at 4.5 mm., $n^{20}D$ 1.4580).

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(19) V. Prelog, E. Cerkovnikov and G. Ustricev, *Ann.*, **535**, 57 (1938).

(20) N. J. Leonard and W. E. Goode, THIS JOURNAL, **72**, 5404 (1950).

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Anal. Calcd. for $C_{11}H_{23}N$: C, 78.03; H, 13.64; N, 8.27; mol. wt., 169.3. Found: C, 77.72; H, 13.88; N, 8.35; mol. wt., 170.

This product was identical with 2-hexylpiperidine (b.p. 80° at 5 mm., $n^{20}D$ 1.4575, 60% yield) prepared by the hydrogenation (over Adams catalyst in acetic acid solution) of 2-hexylpyridine (prepared in 60% yield by the reaction of α-picoline, 55.5 g., 0.60 mole, with *n*-amyl bromide, 30.2 g., 0.20 mole, and sodamide, 27 g., 0.695 mole). The addition product gave a hydrochloride (m.p. 162–163°; m.p. of mixture with authentic sample, 162–163°).

Anal. Calcd. for $C_{11}H_{24}NCl$: N, 6.81. Found: N, 6.66.

Further distillation gave a fraction (2.8 g., b.p. 80–140° at 3 mm., $n^{20}D$ 1.4740, mol. wt. 282) and a residue (4.4 g., average mol. wt. 329) remained.

The Addition of Piperidine to 1-Octene.—Under a pressure of nitrogen (25 lb./sq. in.) in the all-glass pressure apparatus, a reaction mixture with piperidine (382 g., 4.49 moles), 1-octene (40 g., 0.36 mole) and *t*-butyl peroxide (3 g.) was held at 120° for 50 hours. More peroxide (2 g. after 6 hours, 2 g. after 12 hours) was added. Then the reaction mixture was distilled through a 50-plate Podbielniak column to give *t*-butyl alcohol (6.3 g., b.p. 80–82°), unreacted piperidine (359.5 g., b.p. 103–103.5°) and 1-octene (9.5 g., b.p. 118–120°). The residual reaction product left in the still-pot was distilled through a Vigreux column and 2-octylpiperidine (31.7 g., b.p. 89° at 1 mm., $n^{20}D$ 1.4589) was obtained.

Anal. Calcd. for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10; mol. wt., 197. Found: C, 79.34; H, 13.81; N, 7.17; mol. wt., 190.

The identity of this product was confirmed by comparison with 2-octylpiperidine (b.p. 89° at 1 mm., $n^{20}D$ 1.4587) prepared in 95% yield by the hydrogenation over Adams catalyst in acetic acid solution of 2-octylpyridine (prepared, 65% yield, by the reaction of α-picoline, 111 g., 1.2 moles, with *n*-heptyl bromide, 71.6 g., 0.40 mole, and sodamide, 54 g., 1.39 moles).[24] The addition product gave a hydrochloride (m.p. 155–156°; m.p. of mixture with authentic sample, 155–156°).

Anal. Calcd. for $C_{13}H_{28}NCl$: C, 66.77; H, 12.07; N, 5.99. Found: C, 66.53; H, 12.16; N, 5.99.

Its reaction with phenyl isothiocyanate gave a thiourea derivative (m.p. 95°, m.p. of mixture with authentic sample showed no depression).

Anal. Calcd. for $C_{20}H_{32}N_2S$: C, 72.23; H, 9.70; N, 8.42. Found: C, 71.92; H, 9.56; N, 8.45.

Its picrate also was prepared (m.p. 78–80°). *Anal.* Calcd. for $C_{19}H_{30}N_4O_7$: C, 53.51; H, 7.09; N, 13.13. Found: C, 53.31; H, 7.00; N, 13.07.

Further distillation of the reaction product gave a fraction (5.8 g., b.p. 145–155°, $n^{20}D$ 1.4683, mol. wt. 299)) presumed to have resulted from the reaction of one molecule of piperidine with two of 1-octene. A residue (4.5 g., average mol. wt. 448) remained.

2-Octylpiperidine (1 g.) was obtained in small yield when a solution of 1-octene (20.5 g., 0.183 mole) in piperidine (207 g., 2.44 moles) was illuminated for 168 hours with a quartz mercury discharge tube (reaction temperature, 30–55°).

The Addition of Piperidine to Allyl Alcohol.—A reaction mixture containing piperidine (385 g., 4.53 moles), allyl alcohol (19 g., 0.33 mole) and *t*-butyl peroxide (4.5 g., 0.031 mole) was heated in a bomb tube at 122–130° for 48 hours. Distillation gave 2-(3-hydroxypropyl)-piperidine (21.8 g., b.p. 93–95° at 1 mm., $n^{25}D$ 1.4890).[25,26] When hydrogen chloride was passed into a sample of this amino alcohol, its known hydrochloride (m.p. 129–130°) was obtained. A residue (10.7 g., average mol. wt. 283) remained in the distilling flask.

This reaction of piperidine (340 g., 4.0 moles) with allyl alcohol (19 g., 0.33 mole) was also induced with *t*-amyl peroxide (4.5 g., 0.026 mole). This reaction mixture was held at 100° for 48 hours in a 3-necked, 1-liter round-bottomed flask equipped through glass joints with a thermometer and a reflux condenser with its outlet connected with a mercury bubbler. The reaction mixture was then distilled to give 2-(3-hydroxypropyl)-piperidine (2.3 g., b.p. 93–95° at 1 mm., $n^{20}D$ 1.4900) and a residue (4.2 g.). Similar products were obtained in low yield by the reaction of piperidine (180 g., 2.12 moles) with allyl alcohol (9 g., 0.16 mole) induced by 2,2-bis-(*t*-butylperoxy)-butane (1.5 g.) at 95° for 50 hours; 2-(3-hydroxypropyl)-piperidine (1.1 g.) and a residue (2.6 g.) were obtained by distillation.

The procedure previously described[19] was used to prepare δ-coniceine (1-azabicyclo[4.3.0]nonane) from the above 2-(3-hydroxypropyl)-piperidine. This amino alcohol (3 g.) in hydrobromic acid (48%, 60 ml.) was heated in a bomb tube at 100° for 12 hours. Water and excess hydrobromic acid was removed from the reaction mixture under reduced pressure. Recrystallization of the residue from acetone gave 2-(3-bromopropyl)-piperidine hydrobromide (3.7 g., m.p. 180–182°, 62% yield). This product was added over 2.5 hours to sodium hydroxide solution (0.1 *N*, 2000 ml.) held at 50°. After this reaction mixture had cooled, benzenesulfonyl chloride (3 g.) was added. The reaction mixture was then steam distilled until the distillate was no longer basic. The steam distillate (50 ml.) was extracted 3 times with ether. The ether solution was dried over anhydrous sodium sulfate. A small sample of the ether solution was added to a saturated solution of picric acid in ethanol. The picrate of 1-azabicyclo[4.3.0]nonane (m.p. 231–232° after recrystallization from ethanol)[27] precipitated. Distillation of the ether solution gave the amine (0.7 g., b.p. 86° at 32 mm., $n^{21}D$ 1.4697, 61% yield).[26]

The Addition of Piperidine to Allyl Cyanide.—A reaction mixture containing piperidine (374 g., 4.40 moles), allyl cyanide (21 g., 0.31 mole) and *t*-butyl peroxide (5 g., 0.034 mole) was held at 120–124° in a bomb tube for 72 hours. Direct distillation gave presumed 2-(3-cyanopropyl)-piperidine (20.7 g., b.p. 59–60° at 1 mm., $n^{20}D$ 1.4748).

Anal. Calcd. for $C_9H_{16}N_2$: C, 71.00; H, 10.59; N, 18.40; mol. wt., 152. Found: C, 70.82; H, 10.36; N, 18.35; mol. wt., 159.

Its hydrochloride (m.p. 135–136°) was prepared by passing hydrogen chloride into a small portion. *Anal.* Calcd. for $C_9H_{17}N_2Cl$: Cl, 18.79. Found: Cl, 18.51.

Continued distillation gave a fraction (7.1 g., b.p. 100–140° at 1 mm., $n^{20}D$ 1.5024, average mol. wt. 191) and a residue (7.0 g., average mol. wt. 297) remained.

The Addition of γ-Pipecoline to Allyl Alcohol.—A solution containing γ-pipecoline (198 g., 2.0 moles), allyl alcohol (10 g., 0.17 mole) and *t*-butyl peroxide (3 g., 0.02 mole) was held at 123–125° in a bomb tube for 48 hours. Distillation gave a substance presumed to be 2-(3-hydroxypropyl)-4-methylpiperidine (9.1 g., b.p. 99–100° at 1 mm., $n^{20}D$ 1.4875).

Anal. Calcd. for $C_9H_{19}NO$: C, 68.74; H, 12.18; mol. wt., 157. Found: C, 68.80; H, 12.18; mol. wt., 168.

A residue (8.0 g., average mol. wt. 246) remained in the distilling flask.

The Addition of N-Methylpiperidine to 1-Octene.—N-Methylpiperidine (284 g., 2.87 moles), 1-octene (20 g., 0.18 mole) and *t*-butyl peroxide (6 g., 0.041 mole) were heated in a bomb tube at 122–126° for 48 hours. *t*-Butyl alcohol and unreacted N-methylpiperidine and 1-octene were isolated by fractional distillation. The residual product was distilled under vacuum in a Vigreux column to give 2-octyl-N-methylpiperidine (6 g., b.p. 84–85° at 1 mm., $n^{20}D$ 1.4593).

Anal. Calcd. for $C_{14}H_{29}N$: C, 79.54; H, 13.83; N, 6.63; mol. wt., 211. Found: C, 79.44; H, 13.87; N, 6.81; mol. wt., 218.

Further identification of this substance was obtained by comparison with 2-octyl-N-methylpiperidine (23.3 g., b.p. 85° at 1 mm., $n^{20}D$ 1.4590, 75% yield) prepared by the reaction of formic acid (18.9 g., 0.368 mole, 90%) and formaldehyde (35%, 14 g., 0.162 mole) with 2-octylpiperidine (29 g., 0.147 mole) obtained from α-picoline as previously described.[13] Its reaction with methyl iodide gave a methiodide, 2-octyl-N,N-dimethylpiperidinium iodide (m.p. 165°, m.p. of mixture with authentic sample, 165°).

Anal. Calcd. for $C_{15}H_{32}NI$: N, 3.96; I, 35.92. Found: N, 3.70; I, 36.03.

The same derivative was prepared by the reaction of

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methyl iodide with 2-octylpiperidine. Reaction of the addition product with ethyl iodide gave 2-octyl-N-ethyl-N-methylpiperidinium iodide (m.p. 138–139°; m.p. of mixture with authentic sample, 138–139°).

Anal. Calcd. for $C_{16}H_{34}NI$: I, 34.55. Found: I, 34.61.

The remaining distilland was distilled to give a fraction (6.8 g., b.p. 110–170° at 1 mm., $n^{20}D$ 1.4692, average mol. wt. 333), and a residue (8.6 g., average mol. wt. 429) remained.

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Thermal Rearrangement of Triarylmethyl Azides[1]

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A series of triarylmethyl azides of the type p-X-$C_6H_4(C_6H_5)_2CN_3$, where X = H, CH_3O, CH_3, Cl, NO_2 and $N(CH_3)_2$, has been prepared. On heating to 170–190° these substances evolve nitrogen to give mixtures of benzophenone anils. Analyses of the benzophenones from hydrolysis of the anils were used to determine migration aptitudes of the aryl groups. These migration aptitudes are relatively insensitive to the nature of the aryl group—p-anisyl, for example, was only 2.5 times better than phenyl. The unsubstituted azide in solution in dibutyl carbitol, nitrobenzene or hexadecane rearranges by a first-order process, the rate of which is little affected by the nature of the solvent. Similarly, the substituted azides in dibutyl carbitol rearrange at rates which are only slightly influenced by the nature of the substituent. In both series of rate runs there are substantial, but compensating, variations in energies and entropies of activation. Possible explanations of these facts are discussed.

The acid-catalyzed rearrangement of alkyl azides has been studied fairly extensively.[3–7] A thorough investigation of migration aptitudes in this reaction has been carried out by McEwen,[6] who used benzhydryl and 1,1-diarylethyl azides, sometimes as such and sometimes generated *in situ* from the carbinol or the olefin. Migration aptitudes were qualitatively similar to those found in the pinacol rearrangement,[8] but their range was much less. p-Anisyl, for example, had a migration aptitude of 6.5 in the benzhydryl azide rearrangement, compared to 500 in the pinacol rearrangement.

In contrast to the extensive investigations of the acid-catalyzed rearrangement, little is known of the thermal rearrangement. Triphenylmethyl azide rearranges on heating at around 180°, the product being benzophenone anil.[9] In the rearrangement of p-chlorophenyl-(diphenyl)-methyl azide,[9] the migration was claimed to be entirely statistical; *i.e.*, the product was two-thirds that of phenyl migration and one-third that of p-chlorophenyl migration. Our aims were to check this claim, to extend the study to other migrating groups and to determine the kinetics of the reaction. The intermediate I, which would result if nitrogen evolution preceded rearrangement, is the nitrogen analog of the carbenes.[10] Migrations to this uncharged, but electron-deficient, nitrogen atom might be expected to show interesting features.

$$Ar_3C-\ddot{N}: \quad I$$

The only one of the desired azides which had been prepared and adequately characterized prior to the present work was triphenylmethyl azide itself.[11] Of the various methods available for the synthesis of triarylmethyl azides,[12–15] the action of hydrazoic and sulfuric acids on the carbinol[15] proved to be the simplest and also the best. The azides obtained in this manner were low-melting solids with the exception of the p-methoxy azide. This compound refused to crystallize and appeared to contain some unreacted carbinol. Preparations of the carbinol precursors of the azides are described under Experimental. Except for a new preparation of the p-nitro carbinol (treatment of diphenyl-(p-nitrophenyl)-methane with N-bromosuccinimide followed by hydrolysis of the resulting bromide), standard procedures were used.

Experiments on the unsubstituted azide showed that it evolved nitrogen smoothly on heating to 170–200°. The residue, when chromatographed on alumina, gave 75% of benzophenone anil and an amorphous, dark brown material which could not be characterized. The anil was shown independently to be stable to the reaction conditions. The next step was to devise a procedure for analysis of the anil mixtures from the substituted azides. For this purpose the anils were hydrolyzed with a mixture of acetic and hydrochloric acids and the resulting benzophenone mixtures analyzed by comparison of their ultraviolet or infrared spectra with those of synthetic mixtures. Details of the spec-

(1) This work was supported in part by the Office of Ordnance Research, U. S. Army.

(2) National Science Foundation Fellow, 1955–1957.

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