compounds **13**, **14**, **15**, **17**, and **18** are indicated by the modes of association of Figures 1 and 5, that of compound **16** in Figure 2. The D and L assignments of compound **13**, **14**, and **15** have been discussed above; the D assignment of compounds **17** and **18** and the L assignment of compound **16** were known previously.

The ideas developed in these studies about enzyme–substrate associations will be applied to a number of cyclized compounds in a forthcoming article.

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The Oxidative Cleavage of Amines by Aqueous Bromine at 25°

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Abstract: Primary, secondary, and tertiary amines are oxidatively cleaved by aqueous bromine at pH 5–7. An alkyl group is removed and the amine with one less alkyl group is produced. Secondary alkyl groups appear as ketones. The fate of primary alkyl groups depends on the type of amine being oxidized. The propyl group appears as propionaldehyde from tripropylamine, as propionic and pyruvic acids from dipropylamine, and exclusively propionic acid from propylamine. All of these results pertain to runs in which the amine is in excess. The selectivity is low between two alkyl groups, and on this basis the mechanism appears to be loss of proton plus an electron pair (Westheimer mechanism) and thus resembles the oxidative cleavage of ethers. However, the data are not conclusive. The oxidation of tertiary amines by triaryl carbonium ions is briefly examined.

The oxidative cleavage of tertiary amines by halogens has been periodically investigated. Wilstätter and Iglauer[1] were concerned with demethylating N-methyl alkaloids and found that tropidine, tropane, and N-methylpiperidine were demethylated by aqueous chlorine. Aqueous chlorine also cleaved trimethylamine with the formation of N-chlorodimethylamine.[2]

Meisenheimer examined the action of aqueous chlorine and bromine on trimethylamine and triethylamine and recognized that the alkyl group appeared as the aldehyde and that the aldehyde was formed by hydrolysis of an intermediate.[3] The work reported herein contributes only a modest addition to the mechanistic picture given by Meisenheimer. However, in the interim, a free-radical mechanism has been championed,[4] and the cleavage has been conducted under anhydrous conditions[5] and with N-bromosuccinimide,[6,7] all of which overshadow the fact that excellent yields can be achieved under simple aqueous conditions at 25° with ordinary bromine.

Two further studies on oxidative cleavage have been reported. The kinetics of the trimethylamine–aqueous chlorine reaction were examined[8] and the action of aqueous chlorine on $CH_3N(CH_2CH_2Cl)_2$ was studied.[9] Also the history of N-haloamines is germane. The N-chloro- and N,N-dichloroamines are well known. It appears that with aqueous chlorine the various rates and equilibria are such as to allow the isolation of the N-chloroamines.[8,10] The use of these N-chloroamines in converting aromatics to dialkylamino aromatics in 80–100% sulfuric acids[10,11] indicates that they are not readily converted to amines in strong aqueous acids. The reports on N-bromoamines are more limited. Though they have been well characterized from the interaction of amines and bromine in benzene and ether,[12] it is not clear whether they can be isolated from reaction in aqueous solution. An old report claims the isolation of $(CH_3)_2NBr$ in excess alkali in the cold[13] and a recent spectroscopic study is fragmentary.[14]

Products and Yields from Tertiary Amines. The stoichiometry of the oxidative cleavage of tertiary amines by aqueous Br_2 at pH 5 (acetate buffer) is exemplified by the following equation.

$$(CH_3CH_2CH_2)_3NH^+ + Br_2 + 2CH_3CO_2^- \longrightarrow CH_3CH_2CHO\ (90\%) + (CH_3CH_2CH_2)_2NH_2^+ + 2Br^- + 2CH_3CO_2H \quad (1)$$

It is surprising that propionaldehyde is produced because in similar oxidations of ethers and alcohols by aqueous bromine,[15] the intermediate aldehydes could not be detected during the course of the reaction. The formation of propionaldehyde in 90% yield becomes even more surprising in view of comparable rates of

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Table I. Products from the Oxidative Cleavage of Tertiary Amines by Aqueous Bromine at 25° and pH 5 or 6[a]

Tertiary amine	$[R_3N]:[Br_2]$	Time, hr	Products and % yields (based on Br_2)
Trimethyl	4 and 8	24	Formaldehyde, 35 and 70
Triethyl	4 and 8	24	Acetaldehyde, 71 and 89
Tripropyl	2	0.5	Propionaldehyde, 90 Dipropylamine, 70[b]
Tributyl	2	0.5	Butyraldehyde, 84
Triisobutyl	2	0.5	Isobutyraldehyde, 86
Triisopentyl	2	0.5	Isovaleraldehyde, 84
Tribenzyl	2	2	Benzaldehyde, 80
Dimethylpropyl	10	2	Propionaldehyde, 38 Formaldehyde, 12
Dimethylisopropyl	10	4	Acetone, 25 Bromoacetone, 9 Formaldehyde, 16
Dimethylbenzyl	4	1	Benzaldehyde, 70
Dimethylcyclohexyl	4	2	Cyclohexanone, 50 Formaldehyde, 18
Methyldiisopropyl	4	1	Acetone, 17 Bromoacetone, 7 Formaldehyde, 11
Methyldibenzyl	2	0.25	Benzaldehyde, 84
N-Methylpyrrolidine	2	24	Pyrrolidine, 3
N-Methylpiperidine	2	24	Piperidine, 5
N,2-Dimethylpiperidine	2	24	2-Methylpiperidine, 8
N,2,6-Trimethylpiperidine	2	24	2,6-Dimethylpiperidine, 11
N,4-Dimethyldibenzyl	2	0.5	Benzaldehyde, 35 4-Methylbenzaldehyde, 50
N,3-Dimethyldibenzyl	2	0.5	Benzaldehyde, 41 3-Methylbenzaldehyde, 45
N-Methyl-4-chlorodibenzyl	2	0.5	Benzaldehyde, 50 4-Chlorobenzaldehyde, 33
Diisopropylpropyl	2	0.5	Propionaldehyde, 50 Acetone, 21 Diisopropylamine (72)[c] Propylisopropylamine (28)[c]
Dipropylbenzyl	2	0.5	Benzaldehyde, 52 Propionaldehyde, 38 Dipropylamine (58)[c] Propylbenzylamine (42)[c]
Cyclohexyldipropyl	2	0.5	Cyclohexanone, 12 Propionaldehyde, 70
Benzylbis(1-methylbenzyl)	2	2	Benzaldehyde, 75 Acetophenone, 5 1,1′-Dimethyldibenzylamine (94)[c] Benzyl-1-methylbenzylamine (6)[c]

[a] The oxidations for the first 13 compounds were conducted at pH 5 and the remaining 11 compounds were studied at pH 6. [b] Isolated as the benzenesulfonamide. [c] Relative yields.

oxidation of propionaldehyde and tripropylamine. The respective values of k_2 at 25° and pH 5 are 0.0398[16] and 0.099 (Table II).

A variety of tertiary amines has been examined both to determine the generality of the reaction and to determine the direction of cleavage in the case of unsymmetrical amines. The results are summarized in Table I. Yields of less than 80–90% are believed to reflect incomplete reaction or the circumstance that product was isolated from only one direction of cleavage.

The cleavage of unsymmetrical noncyclic amines showed little selectivity in view of the range of alkyl structures studied. What selectivity there was is interpretable in terms of two independent factors. A preference was evident for oxidizing the alkyl group which forms the more stable cation. Thus benzyl was cleaved in preference to primary alkyl group, though not in an overwhelming fashion, and ρ was -0.84 in a limited $\sigma\rho$ study. The second factor was a simple steric factor favoring cleavage of the less hindered alkyl group. This factor opposed and dominated the first factor. For example, benzyl cleaved in preference to α-methylbenzyl and propyl cleaved in preference to isopropyl.

N-Methylpyrrolidine and three N-methylpiperidines gave only small amounts of methyl cleavage under conditions where the reaction was believed to proceed to completion. It is concluded that cleavage predominantly occurs in the direction of ring opening and that the reaction has some promise for degrading alkaloids by ring opening but is not promising for demethylation.

Rate Law. The oxidation of tripropylamine was studied in detail at pH 5 and 25°. The rate law was found to be

$$-d[Br_2]/dt = k_2[Br_2][\text{amine}] \quad (2)$$

This was demonstrated by varying the initial concentra-

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tion of amine from 1 to 4 × 10^{-3} *M* and the initial concentration of bromine from 1.5 to 6.4 × 10^{-4} *M*. The [amine]:[Br_2] ratio varied from 5 to 20. The rate constants calculated from initial rates using eq 2 were all within the range 9.60–10.0 × 10^{-2} l. mol^{-1} sec^{-1} with an average value of 9.90 × 10^{-2}. The [Br_2] was followed iodometrically. As a result, N-bromo compounds would be counted as Br_2.

pH–Rate Profile. The rates for tripropylamine were studied from pH 4 to 7 with and without 0.10 *M* added NaBr. The rates increase from pH 4 to 7 (Table II).

Table II. Oxidation of Tripropylamine by Aqueous Br_2 at 25°

pH[a]	[NaBr]	k_{expt}[b]
4.0	0	0.033
5.0	0	0.099
6.0	0	0.29
7.0	0	0.81
4.0	0.10	0.019
5.0	0.10	0.079
6.0	0.10	0.31
7.0	0.10	0.89

[a] The solutions were buffered with 0.20 *M* acetate. The ionic strength was held at 0.30 by addition of $NaClO_4$. The pH was continuously monitored and $HClO_4$ was added to maintain constant pH within 0.05 unit. [b] The initial stoichiometric concentrations of amine and bromine were 2.00 × 10^{-3} and 2.00 × 10^{-4} *M*. The bromine was titrated iodometrically with sodium thiosulfate solution using starch as an indicator. The rate constant was calculated by eq 2 using data up to 10% completion of the reaction and using the stoichiometric concentrations of amine and bromine.

Qualitatively, this increase can be rationalized in terms of free amine being the reactant and the B–BH^+ equilibrium

$$2.24 \times 10^{-11} = [(Pr)_3N][H^+][(Pr)_3NH^+]^{-1} \quad (3)^{17}$$

Although this is the dominant factor, to this must be added the known equilibria involving Br_2, Br_3^-, and HOBr

$$17 = [Br_3^-][Br_2]^{-1}[Br^-]^{-1} \quad (4)^{18}$$

and

$$6.7 \times 10^{-9} = [HOBr][Br^-][H^+][Br_2]^{-1} \quad (5)^{19}$$

When eq 3–5 are taken into account, the rate constants so calculated are far from constant. Other equilibria and possibly rates appear to be involved. Similar complexities were found in the oxidative cleavage of trimethylamine to formaldehyde by aqueous chlorine.[8] In this latter work it was proposed that the reaction

$$(CH_3)_3N + Cl_2 \longrightarrow (CH_3)_3NCl^+Cl^- \quad (6)$$

was not only significant in affecting trimethylamine concentrations but that it was slow enough to be rate determining under some circumstances.

Effect of Light. The reaction of tripropylamine and aqueous bromine at pH 5 was irradiated with a 250-W sunlamp. No change in rate could be detected compared with the dark reaction. This indicates that a free-radical pathway is not involved or readily introduced.

σ–ρ Study. The cleavage ratios for the three N-methyldibenzylamines (Table I) can be equated to rate ratios. Using standard σ values,[20] ρ was −0.84. The same three cleavage ratios were determined by product analysis for oxidation of the amines by the triphenylmethyl cation in acetonitrile at 50°, a reaction believed to occur by direct hydride transfer.[21] ρ was −2.0 for this hydride transfer.

Primary and Secondary Amines. Propylamine is readily oxidized to propionic acid by aqueous bromine. The reaction was conducted in a phosphate buffer at pH 6 and monitored by nmr spectroscopy. When an equimolar amount of Br_2 was used, the products after 2 hr at 25° were 70% propylamine and 30% propionic acid. This is a 60% yield of propionic acid based on bromine.

When excess bromine is used, propionic acid is the only species present in the aqueous solution after 4 hr. However, the yield is not quite 100% because a minor part of the propylamine is converted to a second liquid, insoluble in water and denser than water. In all runs, no species were ever observed in the nmr spectra of the aqueous solution other than propylamine and propionic acid and this result stands in marked contrast to the behavior of tertiary amines.

Somewhat different results were obtained with dipropylamine. After 12 hr with excess bromine, the water soluble products consisted entirely of pyruvic and propionic acids in the ratio 3:7. A small amount of a water-insoluble layer formed that was denser than water.

It is evident from these preliminary studies that propylamine and dipropylamine are rapidly oxidized and that conditions could probably be found for obtaining pyruvic or propionic acids in good yields from dipropylamine.

Isopropylamine was also studied at pH 6, but in an acetate buffer. Equimolar bromine was added. After 4 hr at 25°, the bromine had disappeared. The ketonic products were converted to the 2,4-dinitrophenylhydrazones by direct addition of sulfuric acid and reagent to the reaction mixture. Analysis by nmr showed that acetone and bromoacetone had been formed in yields of 48 and 3%. Similarly diisopropylamine formed acetone and bromoacetone in yields of 63 and 10%.

Synthetic Utility. In view of the rapidity of all of the above reactions, the generally good to excellent yields, and the simplicity of reagents and operation, it is surprising that these bromine oxidations of amines have had such limited use for the degradation of alkaloids. We suspect that failure to buffer the reactions at pH 6 has led to the reaction mixture becoming acidic with concomitant very slow rates and the incursion of brominated products. Attention to this minor detail should make the reaction more attractive for synthetic and degradative purposes.

Another factor inhibiting the use of these reactions may have been a general impression that N-bromoamines are the end products. Although they probably form, they do not accumulate.

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(18) M. Eigen and K. Kustin, *ibid.*, **83**, 1945 (1961).
(19) This was calculated from the value given at 20° in ref 18 and the temperature coefficient (H. A. Liebhafsky, *ibid.*, **61**, 3513 (1939)). Unfortunately, ref 15 gives this equilibrium constant as 9 × 10^{-9} which is in error. This error does not significantly affect the data or conclusions in ref 15.
(20) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).
(21) H. Meerwein, V. Hederich, H. Murschel, and K. Wunderlich, *Ann.*, **635**, 1 (1960); R. Damico and C. D. Broaddus, *J. Org. Chem.*, **31**, 1607 (1966).

The oxidative cleavage is not restricted to tertiary amines in contrast to several other methods, for example, the oxidative cleavage by nitrous acid.[22] Amides are inert and this provides a means of protecting and re-forming primary and secondary amines. In the case of tertiary amines, the reaction has some potential for the synthesis of aldehydes.

On the debit side, many aromatic rings, particularly the alkoxy-substituted type so prevalent in alkaloids, may be brominated. Of course, the reaction can be continued on such brominated substrates. Somewhat the same story holds for double bonds where bromine addition may be competitive.

Mechanism. Despite the considerable amount of data presented, the mechanism is not clear. The insensitivity to electronic effects, the rate law, the qualitative aspects of the pH–rate profile, the insensitivity to light, and the small negative ρ all point to a mechanism similar to that proposed for the oxidation of ethers by aqueous bromine.[5] The essential features of this mechanism were the loss of the α hydrogen as H^+ and the abstraction of an electron pair by Br_2. The electron pair is donated by the oxygen in ethers and by the nitrogen in the amines.

What are not explained by the above picture are the complexities in the pH–rate profile and the markedly different types of products from primary, secondary, and tertiary amines. We can only speculate that N-bromoamines and eneamines may be intermediates that affect product ratios and such questions are left for future study.

Other Oxidations of Amines. The oxidative cleavage of tertiary amines by nitrous acid[22] closely resembles the Br_2 oxidations. In both cases, the Westheimer mechanism (loss of H^+ and electron pair) was favored. A cyclic transition state was proposed for the nitrous acid oxidation,[22] and a similar one can be written for the Br_2 oxidation. However, we feel that in neither case is there any direct evidence leading to a choice between such cyclic transition states and simply solvent abstraction of H^+.

Tertiary amines have been oxidized by a variety of reagents including lead tetraacetate, mercuric acetate, manganese dioxide, permanganate, tetranitromethane, peroxides, oxygen, sulfur, and ozone.[23]

Experimental Section

Nmr Spectra. All spectra were recorded on a Varian A-60 spectrometer. Field homogeneity was adjusted with a degassed sample of bromoethane until resolution was better than 0.5 cps. All band positions are given in parts per million (ppm) downfield from tetramethylsilane (δ). In aqueous solution, tetramethylammonium ion (3.10 ppm) was used as a secondary standard.

Oxidation of Amines. The general procedure was to dissolve 0.10–0.01 mol of amine in 50 ml of 0.40 *M* acetate buffer. The pH was adjusted with concentrated hydrochloric acid and Br_2 added. The solution was stirred at 25° until the Br_2 disappeared.

Analysis of Aldehydes and Ketones. The reaction mixture was added directly to 300 ml of 3 *M* hydrochloric acid containing a two-fold excess of 2,4-dinitrophenylhydrazones. The precipitated dinitrophenylhydrazones (DNP's) were filtered, dried, and weighed. The aliphatic examples were analyzed by nmr spectroscopy of a dichloromethane solution of the DNP's. A doublet at 9.06 (J = 2.5 cps) was common to all DNP's (and dinitrophenylhydrazine). The nmr bands of the DNP's were acetone, 2.10 and 2.19 (areas 1:1); bromoacetone, 2.25 and 4.27 (areas 3:2, either only one *cis–trans* isomeric forms or the spectra of the two isomers are not resolved); cyclohexanone, 0.88 and 1.50 (broad bands) (areas 6:4); formaldehyde, 7.12 and 7.32 (areas 1:1); propionaldehyde, 1.21 (triplet, J = 7.0 cps), 2.44 (complex multiplet), and 7.63 (triplet, J = 5.0 cps) in areas 3:2:1 (either only one isomer or isomers not resolved).

Where benzaldehyde was the only aromatic aldehyde formed, the DNP's of the aliphatic aldehydes and ketones could be extracted by dichloromethane and the residual DNP of benzaldehyde checked for purity by its melting point.

Where competition produced two substituted benzaldehydes or acetophenone, the total yield was determined from the weight of DNP and the relative proportions by gas chromatography of the aldehydes and acetophenone. In these cases the carbonyl compound was isolated by adjusting the pH to 4 and extracting with ether. The gas chromatogram was conducted on a Barber-Colman series 5000 equipped with flame ionization detector. The U-shaped column was 12 ft in length and 4 mm i.d. Nitrogen was the carrier gas and the packing was 10% ethylene glycol succinate polyester on 100–120 mesh Gas Chrom P.[24] The same proportionality between weight and detector response was found for benzaldehyde, its 3- and 4-methyl derivatives, and acetophenone. For 4-chlorobenzaldehyde, the detector response had to be multiplied by 1.33 to obtain the same proportionality.

The oxidations of amines by triphenylmethyl tetrafluoroborate[25] required a slightly different isolation procedure. After completion of the reaction in acetonitrile at 50°, the solvent was removed and the triphenylmethane extracted with ether. The immonium salt, which is insoluble in ether, was hydrolyzed at a pH of 4 for 24 hr. The aldehyde was then isolated and analyzed as with the bromine oxidations.

Analysis of Amines. The procedure was the same as that used with the benzaldehydes except that the packing was Carbowax (polyethylene glycol) containing potassium hydroxide on 100–120 mesh Gas Chrom Q or Chromosorb W.[24] Proportionality between weight and detector response was demonstrated with authentic samples except in the case of isomers where it was generally assumed. One precaution that was generally taken was to inject two different size samples. The same analysis on both samples assured that the sample sizes were within the range of linear response.

Clarke–Eschweiler Synthesis of Amines. The N-methylation of primary and secondary amines with formaldehyde and formic acid is well known.[26] The following amines were prepared by this method and were distilled from sodium before use.

N,N-Dimethylisopropylamine was obtained from isopropylamine in 63% yield, bp 64–64.5° (lit.[27] 67.5°). The nmr spectrum of a CCl_4 solution had a doublet at 0.96 (J = 7.0 cps), a singlet at 2.14, and a heptet at 2.54 (J = 7.0 cps) in the ratios 6:6:1.

N-Methyldiisopropylamine was obtained from diisopropylamine in 70% yield, bp 108–110° (lit.[28] 112°). The nmr spectrum of a CCl_4 solution had a doublet at 0.97 (J = 7.0 cps), a singlet at 2.07, and a heptet at 2.82 (J = 7.0 cps) in the ratios 12:3:2.

N,N-Dimethylpropylamine was obtained from propylamine in 65% yield, bp 70–71° (lit.[29] 73°). The nmr spectrum of a CCl_4 solution had a triplet at 0.91 (J = 7.0 cps), an overlapping complex multiplet at 1.50 and singlet at 2.22, and a triplet at 2.35 (J = 6.5 cps) in the ratios 3:8:2.

N-Methyldipropylamine was obtained from dipropylamine in 70% yield, bp 113–115° (lit.[30] 117°). The nmr spectrum of a CCl_4 solution had a triplet at 0.89 (J = 7.0 cps), an overlapping complex multiplet at 1.43 and singlet at 2.12, and a triplet at 2.33 (J = 6.5 cps) in the ratios 6:7:4.

N,2-Dimethylpiperidine was obtained from 2-methylpiperidine in 68% yield, bp 115–117° (lit.[31] 118°). The nmr spectrum of a CCl_4 solution had a doublet at 1.00 (J = 6.0 cps), each component

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(23) The leading references are included in the Ph.D. Thesis of R. E. Fruit, Jr., The Pennsylvania State University, 1967.

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(27) A. Skita and F. Keil, *Monatsh.*, **53/54**, 753 (1929).

(28) J. H. Wotiz, C. A. Hollingworth, and A. W. Simon, *J. Org. Chem.*, **24**, 1202 (1959).

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(30) M. Passon, *Ber.*, **24**, 1681 (1891).

(31) J. A. Barltrop and D. A. H. Taylor, *J. Chem. Soc.*, 108 (1951).

a doublet with J = 2.0 cps, a broad band at 1.0–2.0, a singlet at 2.15, and a broad band at 2.4–3.0 in the ratios 3:6:3:3.

N,2,6-Trimethylpiperidine was obtained from 2,6-dimethylpiperidine in 66% yield, bp 143–146° (lit.[32] 149°). The nmr spectrum in CCl_4 solution had a doublet at 1.03 (J = 6.0 cps), a broad band at 1.0–2.0, a singlet at 2.14, and a broad band at 2.2–2.8 in the ratios 6:6:3:2.

Synthesis of Amines by Alkylation. Equivalent amounts of amine, alkyl halide, and Na_2CO_3 were stirred in glycerol under N_2 at 100–150° for 24 hr. The amine was isolated by drowning in water, ether extraction, drying over KOH, and distilling from sodium.

N-Methyldicyclohexylamine was obtained from dicyclohexylamine and iodomethane in 75% yield, bp 145–150° (22 mm) (lit.[33] 150° (20 mm)). The nmr spectrum of a CCl_4 solution had two broad overlapping bands at 1.22 and 1.66, a singlet at 2.19, and a broad band at 2.43 in the ratios 20:3:2.

N-Methyl-4-chlorodibenzylamine was obtained from 4-chlorobenzyl chloride and N-methylbenzylamine in 65% yield, bp 181–185° (18 mm), hydrochloride mp 144–146° (lit.[34] 146.5°). The nmr spectrum of a CCl_4 solution had singlets at 2.10, 3.36, 3.40, and 7.25 in the ratios 3:2:2:9.

N,4-Dimethyldibenzylamine was obtained from 4-methylbenzyl chloride and N-methylbenzylamine in 60% yield, bp 171–175° (18 mm), hydrochloride mp 158–160° (lit.[34] 162°). The nmr spectrum of a CCl_4 solution had singlets at 2.13, 2.30, and 3.46 and a complex multiplet at 7.25 in the ratios 3:3:4:9.

N,3-Dimethyldibenzylamine was obtained from 3-methylbenzyl chloride and N-methylbenzylamine in 60% yield, bp 156–158° (11 mm).

Anal. Calcd for $C_{16}H_{19}N$: C, 85.3; H, 8.5. Found: C, 85.8; H, 8.5.

The nmr spectrum of a CCl_4 solution had singlets at 2.12 and 2.32, two overlapping singlets at 3.42 and 3.44, and a complex multiplet at 7.21 in the ratios 3:3:4:9.

N,N-Dipropylcyclohexylamine was obtained from 1-bromopropane and cyclohexylamine in 60% yield, bp 101–102° (20 mm).

Anal. Calcd for $C_{12}H_{25}N$: C, 78.6; H, 13.7. Found: C, 78.8; H, 13.6.

The nmr spectrum of a CCl_4 solution had a triplet at 0.84 (J = 7.0 cps), a complex series of bands from 1.9 to 2.9, and an overlapping triplet at 2.32 (J = 7.0 cps) and an underlying broad band in the ratios 6:14:5.

N-Isopropylpropylamine (bp 93–96°, lit.[35] 98°), N-isopropylbenzylamine (bp 100–103° (20 mm), lit.[36] 50–55° (0.8 mm)), and N-propylbenzylamine (bp 111–114° (22 mm), lit.[36] 47–55° (0.2 mm)) were prepared from isopropylamine or propylamine and the appropriate bromide or chloride in small amounts for use in identification of gas chromatogram bands. The nmr spectra of all three amines were in accord with their structure.

Reduction of N,N-Dialkylamides. Several of the amines were prepared by reduction of the N,N-dialkylamides with a 50% excess of $LiAlH_4$ in ether at 35° for 2 days.

N-Propyldiisopropylamine was obtained from N,N-diisopropylpropionamide in 70% yield, bp 41–42° (18 mm) (lit.[33] 150°). The nmr of a CCl_4 solution had an overlapping doublet at 0.98 (J = 6.5 cps) and triplet at 0.96 (J = 6.5 cps), a complex multiplet at 1.37, a triplet at 2.37 (J = 6.5 cps), and a heptet at 2.99 (J = 6.5 cps) in the ratios 15:2:2:2.

N,N-Dipropylbenzylamine was obtained from N,N-dipropylbenzamide in 85% yield, bp 139–140° (42 mm) (lit.[37] 248°). The nmr spectrum in CCl_4 had a triplet at 0.85 (J = 6.5 cps), a complex multiplet at 1.45, a triplet at 2.37 (J = 6.5 cps), a singlet at 3.51, and a complex multiplet at 7.25 in the ratios 6:4:4:2:5.

N,N-Diisopropylbenzylamine was obtained from N,N-diisopropylbenzamide in 75% yield, bp 118–120° (34 mm).

Anal. Calcd for $C_{13}H_{21}N$: C, 81.6; H, 11.1. Found: C, 82.1; H, 10.8.

The nmr spectrum in CCl_4 had a doublet at 1.01 (J = 6.5 cps), a heptet at 2.99 (J = 6.5 cps), a singlet at 3.58, and a complex multiplet at 7.18 in the ratios 12:2:2:5.

N-Benzylbis(α-methylbenzyl)amine was obtained from N,N-bis(α-methylbenzyl)benzamide in 55% yield, mp 75–76° from ethanol.

Anal. Calcd for $C_{23}H_{25}N$: C, 87.6; H, 8.0. Found: C, 87.0; H, 7.9.

In this case, the reduction was conducted for 72 hr at 48° in a refluxing mixture of ether and dioxane. The nmr spectrum in CCl_4 had a doublet at 1.32 (J = 7.0 cps), a singlet at 3.55, a quartet at 3.85 (J = 7.0 cps), and a slightly broadened singlet at 7.23 in the ratios 6:2:2:15.

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