Summary

Taurine, 2-amino-ethylsulfonic acid, has been prepared in fair yields by converting ethylene bromide to sodium 2-bromo-ethylsulfonate and treating this product with aqueous ammonia.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF PHARMACOLOGY OF JOHNS HOPKINS UNIVERSITY]

THE INFRA-RED ABSORPTION SPECTRA OF ORGANIC DERIVATIVES OF AMMONIA. V. PRIMARY, SECONDARY AND TERTIARY ALKYL AMINES

BY FREDERICK K. BELL[1]

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Introduction

All of the ammonia derivatives thus far examined in this series of studies[2] contained the aryl group and, with the exception of the phenyl amines and naphthylamine, were of the mixed aryl-alkyl type.

The present communication is concerned with the examination of the purely aliphatic amines. It was hoped that the results of this investigation, in conjunction with those already obtained in the case of the pure aryl amines, would be of assistance in the interpretation of the absorption spectra of the mixed amines previously examined. This expectation has been at least partially fulfilled.

The absorption spectra, between 1.0 and 12.0μ, of three series (*n*-propyl, *n*-butyl and *iso*-amyl) of primary, secondary and tertiary amines are presented and discussed in this communication.

Experimental Part

The same experimental procedure as previously described has been followed in the present work. Since all of the substances examined are liquids, the measurements were made at room temperature. In this connection it appears desirable to mention a precaution which should be taken in the examination of liquids in the open type of absorption cell as employed in this work. Considerable evaporation of the liquid may take place depending, of course, on the boiling point of the liquid in question, and liquid must be added from time to time in the course of the examination. This procedure was found to be necessary in the case of several compounds in the present study.

The specimens of mono-, di- and tri-*n*-propylamine, mono-, di- and tri-*n*-butylamine and mono-, di- and tri-*iso*-amylamine were obtained from

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[1] E. R. Squibb and Sons Fellow.

[2] Bell, THIS JOURNAL, (a) **47**, 2192, 3039 (1925); (b) **48**, 813, 818 (1926).

the Eastman Kodak Company. They were labeled "highest purity" and were used as obtained in original glass-sealed containers.

The absorption spectra of these compounds are shown graphically in Figs. 1 to 9, in which the percentage transmission has been plotted against the wave length in microns. In every case the thickness of the absorbing layer was 0.025 mm., as indicated on each curve by the value of T.

Discussion

The infra-red absorption spectrum of only one of the simple alkyl amines has been recorded in the literature, namely, triethylamine, in Coblentz' monograph.[3]

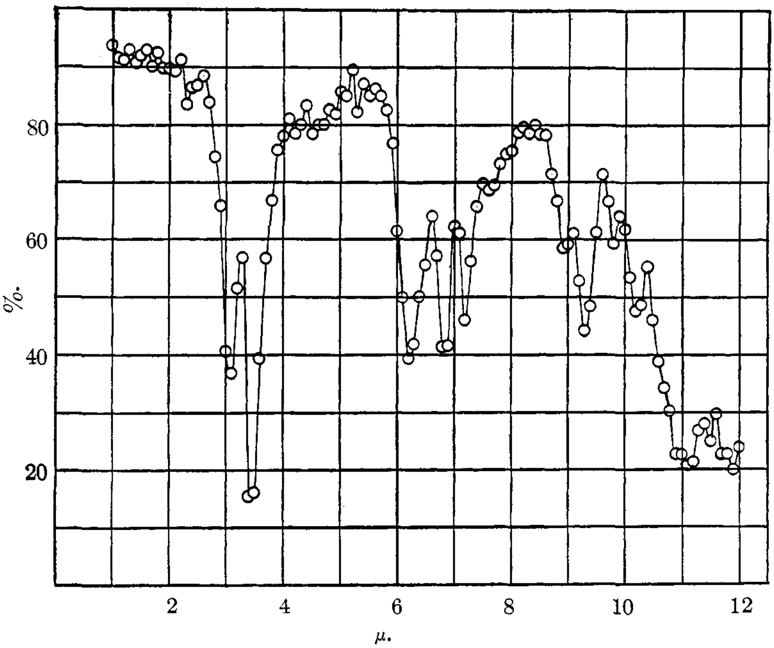

Fig. 1.—n-Propylamine; T = 0.025 mm.

The curves in Figs. 1 to 9 show certain general similarities. The general transparency of the nine substances is of the same order of magnitude, with the possible exception of di-n-butylamine. However, between 10.0 and 12.0μ the three mono derivatives (Figs. 1, 4 and 7) show a marked similarity in opacity, as contrasted with the relatively high degree of transparency of the other derivatives in the same region. No definite influence which can be attributed to increase in molecular weight is to be noticed.

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[3] Coblentz, *Carnegie Inst. Pub.*, **35**, 63 (1905).

In the region of 3.45μ, the characteristic band of the methyl group is sharply defined in each case with marked regularity in intensity. Similarly, in each curve there appears a band of diminished intensity at 6.85μ. Coblentz found this band in numerous compounds of different chemical structure. If we assume an harmonic relation between this band and the 3.45μ band, its presence is to be attributed to the same origin, that is, the methyl group.

It will be noticed also that a sharply defined band appears in each curve in the region of 7.25μ, its position varying from 7.2 to 7.3μ. With the possible exception of a band appearing with a fair degree of constancy in the region of 9.3μ, no consistent similarity of the absorption curves is apparent in the longer wave lengths. This 9.3μ band was found consistently by Coblentz in his examination of petroleum distillates.[3]

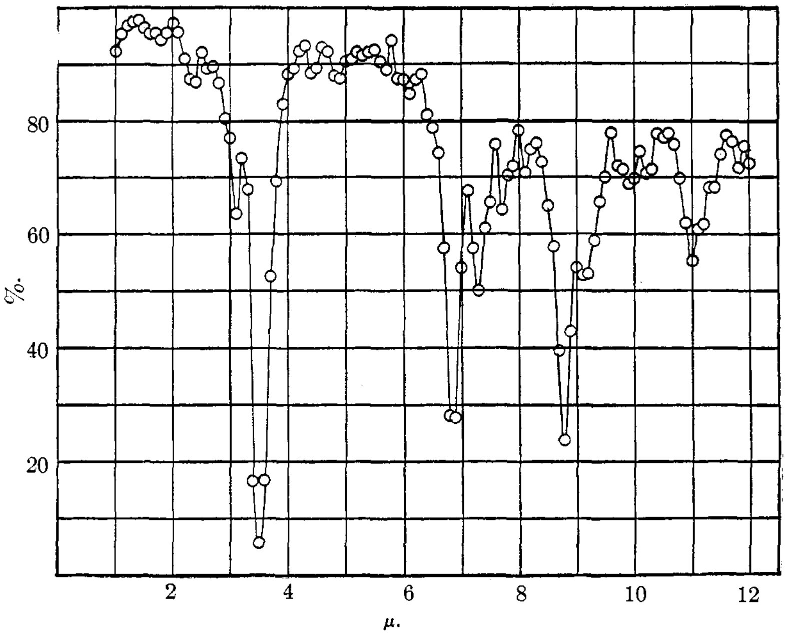

Fig. 2.—Di-*n*-propylamine; T = 0.025 mm.

As in the case of all of the ammonia derivatives which have been previously examined, the region between 3.0 and 4μ is of particular interest in the present study also. As has been noted above, the 3.45μ band remains strikingly constant in intensity, which appears to be independent of the molecular weight of the substituent alkyl group and also the number of hydrogen atoms of the ammonia molecule which have been substituted.

In the three primary amines (*n*-propyl, *n*-butyl and *iso*-amyl), the ammonia band is sharply resolved at 3.05μ, its intensity being less than that of the 3.45μ band in each case. In the secondary amines (Figs. 2, 5 and 8), its location remains unchanged but its intensity is markedly decreased. This band has practically disappeared in the curves for the three tertiary amines (Figs. 3, 6 and 9) and is also absent in Coblentz' curve for triethylamine.

It is thus seen that the qualitative differentiation between primary and secondary and tertiary amines, as previously found, is valid in the case of the alkyl amines.

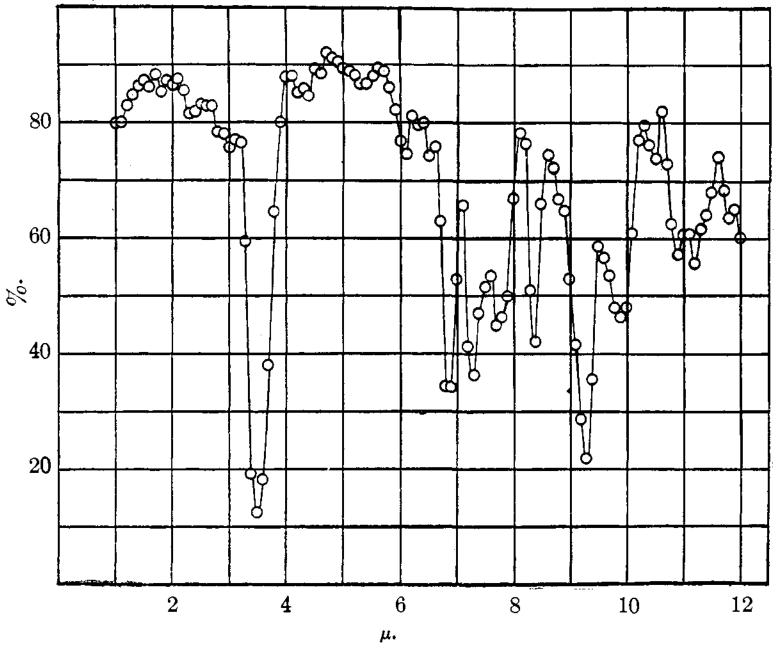

Fig. 3.—Tri-*n*-propylamine; $T = 0.025$ mm.

Salant[4] has examined the absorption spectra of di- and tri-*n*-propylamine, di- and tri-*n*-butylamine and di- and tri-*iso*-amylamine in the restricted region of 2.5 to 4.0μ. In that region of the present curves, there is good agreement with his measurements. It is apparent, however, that Salant used considerably thicker layers of the absorbing materials than those employed in the present study.

Another region of interest in the absorption spectra of the alkyl amines is at 6.25μ. In an earlier communication it was suggested that the[2a] deep ammonia band, which Coblentz locates at 6.1μ, was also present in the spectra of organic derivatives of ammonia. It was pointed out that the absorption in that region cannot be readily interpreted when the benzene nucleus is present, since that nucleus has a characteristic ab-

[4] Salant, *Proc. Nat. Acad. Sci.*, **12**, 74 (1926).

sorption at 6.25μ. In the present curves it is to be expected that the conditions in that region are greatly simplified.

In the case of the three primary amines (Figs. 1, 4 and 7) a well-defined band appears at 6.25μ, while the secondary and tertiary amines in Figs. 2, 3, 5, 6, 8 and 9 (and also in Coblentz' curve for triethylamine) show very little or no characteristic absorption at that point. There is, therefore, a marked diminution in the intensity of this band in passing from the primary to the secondary alkyl amine, but a slight change or none is to be noticed in the transition from the secondary to the tertiary amine; the examination of thicker layers of these substances might reveal a more pronounced difference.

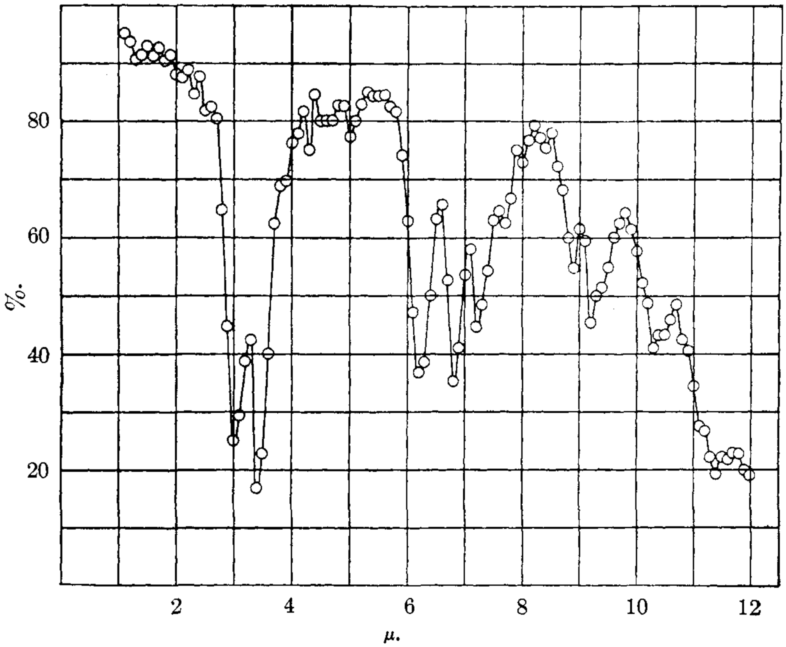

Fig. 4.—*n*-Butylamine; $T = 0.025$ mm.

Salant, assuming the presence of the 6.1μ ammonia in amines,[4] suggests that the 3.0μ ammonia band is the first harmonic of the 6.1μ band. Ellis,[5] on the other hand, has shown, from his examination of aniline and ten mono- and dialkyl anilines as far as 2.8μ, that absorption bands occurring at 1.47μ and 1.04μ are characteristic of the nitrogen to hydrogen bond and that the vibrations corresponding to these two bands and that at 2.8μ, as found by the present author in an examination of the same compounds, form a three-membered parabolic series.

If we assume a shifting of the 6.1μ ammonia band to 6.25μ, the absorp-

[5] Ellis, This Journal, 49, 347 (1927).

tion curves of *n*-propyl, *n*-butyl and *iso*-amylamine confirm Salant's hypothesis. However, a more thorough examination of the secondary and tertiary alkyl amines in this region will be necessary in order to demonstrate definitely the presence or absence of characteristic absorption.

For present purposes, the significance of the 6.25μ band is quite definite. The absorption in this region permits a ready differentiation between mono-alkyl amines and di- or tri-alkyl amines. This differentiation should be especially useful in the examination of those compounds which contain the hydroxyl group, which has a pronounced characteristic absorption at 3.0μ. An instance of the complications that may exist in this region (3.0μ) is shown by the author's absorption curves of the alkaloids containing the tropan nucleus.[6]

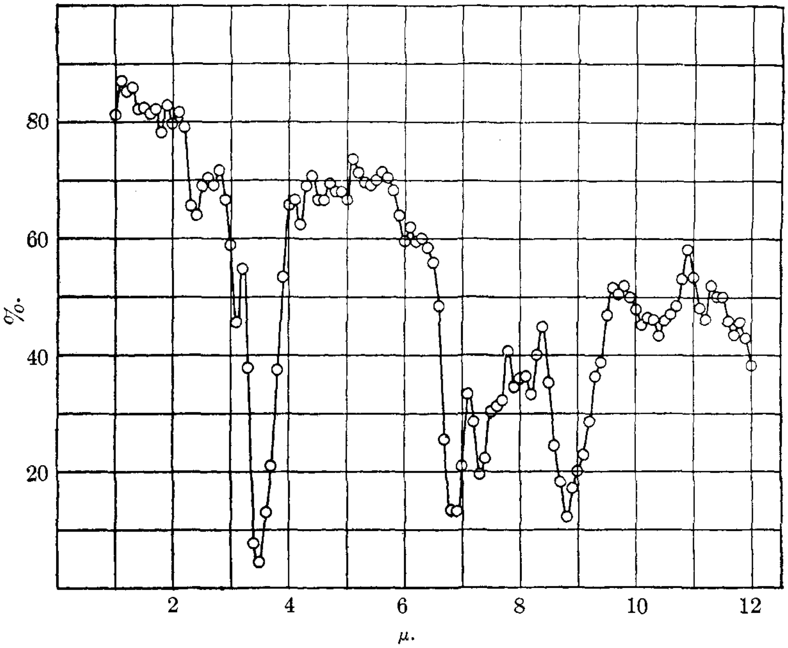

Fig. 5.—Di-*n*-butylamine; $T = 0.025$ mm.

Since the publication of the preceding paper of this series, it has come to the author's attention that a number of pertinent communications by Bonino had been inadvertently overlooked. Bonino[7] suggests that the absorption occurring between 2.5 and 3.9μ is caused by linear oscillators formed of hydrogen atoms which oscillate around their position of equilibrium. If the hydrogen is united to one atomic species, for

[6] Bell, *J. Pharmacol.*, **29**, 533 (1926).

[7] Bonino, *Gazz. chim. ital.*, **53**, 555, 575, 583, 591 (1923); **54**, 357, 465 (1924); **55**, 335, 341, 576 (1925); **56**, 278, 286, 292, 296 (1926).

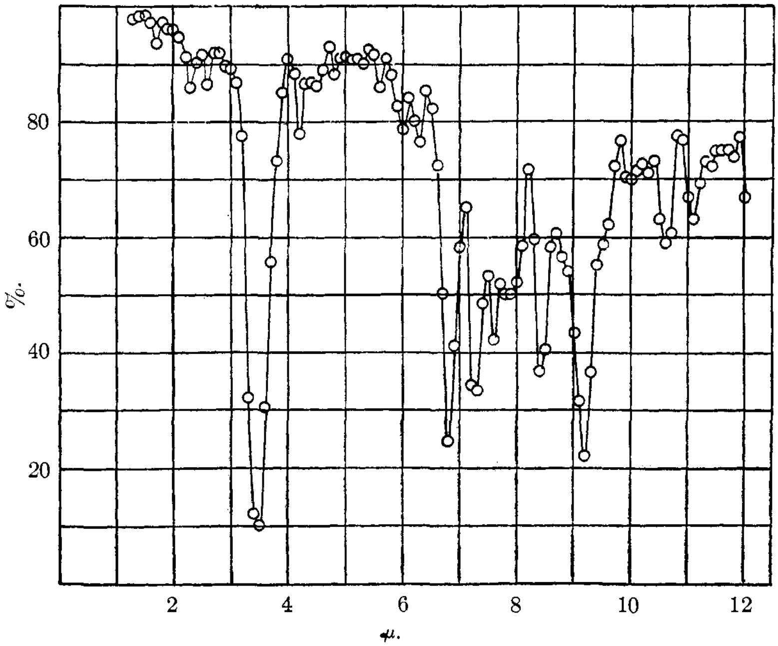

Fig. 6.—Tri-*n*-butylamine; $T = 0.025$ mm.

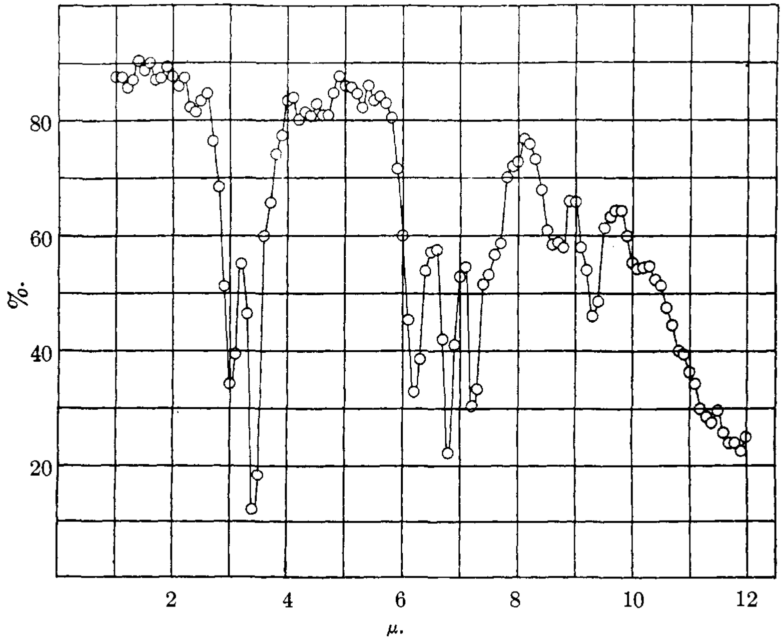

Fig. 7.—*Iso*-amylamine; $T = 0.025$ mm.

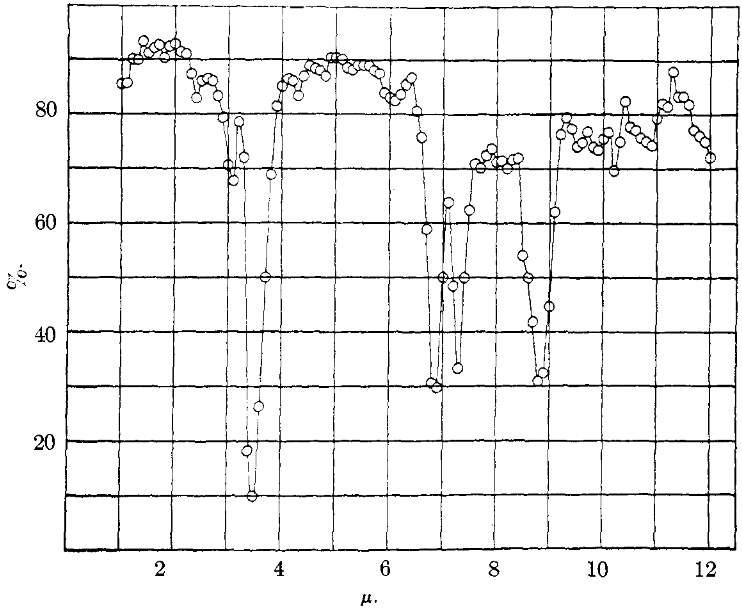

Fig. 8.—Di-*iso*-amylamine; $T = 0.025$ mm.

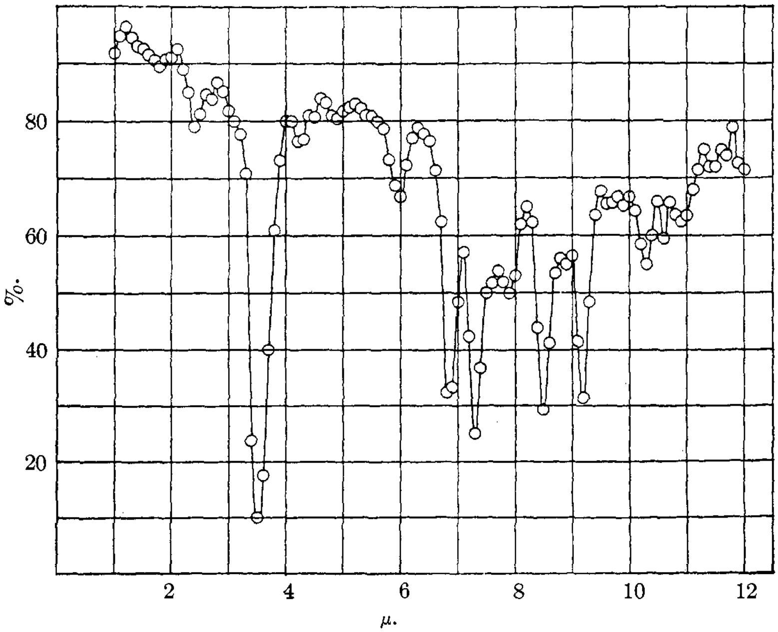

Fig. 9.—Tri-*iso*-amylamine; $T = 0.025$ mm.

example, carbon, oxygen or nitrogen, a simple band of constant location results, as in methane, water or ammonia. On the same basis, we should expect the presence of two bands in this region for such compounds as methyl alcohol or methylamine.

In his examination of the infra-red absorption spectra of halogen derivatives of ethylene and ethane (in which the number of carbon atoms is constant), Bonino found that the absorption band was always at 3.51μ. Its intensity varied, however, and it was entirely absent in tetrachloroethylene and hexachloro-ethane; furthermore, he observed that the coefficient of maximum absorption of this band follows quantitatively the variation in the number of hydrogen atoms, independently of the number of carbon atoms present. The exact location of this band in compounds of different chemical composition is determined, according to Bonino, by intermolecular action.

That these conclusions, developed by Bonino specifically for the case of the carbon to hydrogen bond, are likewise applicable to the nitrogen to hydrogen bond, as suggested by him, appears to be substantiated, at least qualitatively, by the experimental data of this series of studies. Preliminary work by the present author on the examination of some alkyl and aryl mercaptans, sulfides and disulfides points to a similar behavior for the hydrogen to sulfur bond.

Summary

1. The infra-red absorption spectra of mono-, di- and tri-*n*-propylamine, mono-, di- and tri-*n*-butylamine and mono-, di- and tri-*iso*-amylamine have been examined between 1.0 and 12.0μ.

2. The qualitative differentiation between primary and secondary and tertiary amines, by means of the intensity of the characteristic absorption band in the region of 3.0μ, has been found to be valid in the case of the alkyl amines.

3. Primary alkyl amines may be qualitatively differentiated from secondary or tertiary alkyl amines by the absorption in the region of 6.2μ. The significance of this differentiation, which fails in the presence of the aryl group, has been indicated.

BALTIMORE, MARYLAND

NOTES

A Grignard Starter.—Very often when preparing a Grignard reagent, addition of the halide fails to start the reaction. This is true of readily prepared reagents.

The writer has been quite successful in touching off such reaction mixtures by adding a small grain of anhydrous aluminum bromide. The bromide is quickly prepared by warming a few grains of aluminum in a