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 tetrachloro-ethylene 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.

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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 dish and pouring in some bromine, again warming to volatilize the excess. The mixture glows and fumes and the product must be used immediately. Anhydrous aluminum chloride[1] has also been successfully employed a few times.

The method has not been applied to any of the very difficult preparations.

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The Chloromethylacetophenones.—In connection with some work on the condensation of benzil and substituted acetophenones, we have had occasion to prepare the 2-chloro-5-methyl and 4-chloro-3-methyl derivatives from *p*-chlorotoluene and *o*-chlorotoluene, respectively. These ketones have been reported once previously by Claus.[1] He made them by the action of acetyl chloride on the chlorotoluene in the presence of anhydrous aluminum chloride; his yields were very poor and the ketones boiled over a considerable range; furthermore, he did not analyze them because he realized they were impure. He made the oximes, however, and proved the structure of the ketones by oxidation to the corresponding chlorotoluic and chlorophthalic acids.

By the use of acetic anhydride instead of acetyl chloride[2] we have obtained the ketones nearly constant boiling after one distillation, the 3-chloro-4-methyl derivative in a yield of 70% and the 2-chloro-5-methyl derivative in a yield of 34%. Claus had great difficulty in preparing even small amounts of the latter. We have determined the boiling points and refractive indices of both the ketones; they distil without decomposition at atmospheric pressure, forming colorless oils that very slowly take on a yellow tinge in the light. They have a very faint odor suggestive of acetophenone.[3]

Ketones	B. p., °C.	Press., mm.	n_D^{25}	Anal. Calcd. C, %	H, %	Found C, %	H, %
2-Chloro-5-methylacetophenone	245.8–246.0	760.1	1.5419	64.1	5.3	63.9	5.4
4-Chloro-3-methylacetophenone	254.2–254.4	753.4	1.5521	64.1	5.3	64.0	5.3

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[1] Hesse, *Ber.*, **39**, 1127 (1906).

[1] Claus, *J. prakt. Chem.*, [2] **43**, 356 (1890); **46**, 26 (1892).

[2] Noller with Adams, THIS JOURNAL, **46**, 1889 (1924).

[3] The boiling points were determined with the mercury column of the thermometer wholly immersed in the vapor.