line fatty acid ester. A molecular proportion of the desired phenacyl or halogen phenacyl bromide was then introduced, and the reaction mixture boiled under a reflux condenser with the addition of sufficient alcohol to keep the reaction product in solution. After being heated for one hour, the flask was cooled, and the separated solid recrystallized from dilute alcohol to constant melting point. Analysis for halogen by the Parr bomb proved the compounds to be the expected esters.

All the phenacyl compounds prepared are colorless crystalline solids, the majority of them exhibiting a marked luster. This property decreases with increase in molecular weight, and a tendency is noted toward decrease in crystal size with increase in molecular weight.

Approximate solubility determinations were made by removing a 25-cc. portion of the saturated solution from solutions maintained at 20 and 25° in suitable constant temperature baths and drying to constant weight.

The data which have been accumulated are included in Table I.

Summary

Phenacyl, *p*-chlorophenacyl and *p*-bromophenacyl esters of lauric, myristic, palmitic, stearic, arachidic and lignoceric acids have been prepared and described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

AMMONOLYSIS OF KETONES

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In general the ammono ketones[1] have been prepared by the action of ammonia or substituted ammonia on ketones or dihalogen compounds of the formula R_2CX_2, where X represents halogen,[2] and by the reaction of Grignard reagents and the nitriles.[3]

Since the reaction of ammonia with ketones is obviously a reversible

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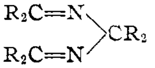
[1] For a discussion of the terms and methods used in this paper see Strain, THIS JOURNAL, **49**, 1558 (1927), and the included references to Franklin and his co-workers.

[2] Pauly, *Ann.*, **187**, 199 (1877); Thomae, *Arch. Pharm.*, **243**, 395 (1905); Hantzsch and Kraft, *Ber.*, **24**, 3516 (1891).

[3] Moureu and Mignonac, *Compt. rend.*, **156**, 1801 (1913); *ibid.*, **158**, 1395 (1914). Of the three types of ammono ketones which are theoretically possible, only those corresponding to the aldimines and to the ammono aldehyde-acetals are known [Strain, THIS JOURNAL, **50**, 2218 (1928)].

$R_2C{=}NH$ Ketimine (known)

$R_2C{=}NR$ Ketimine (known)



$$\begin{matrix} R_2C{=}N \\ R_2C{=}N \end{matrix}\Big\rangle CR_2$$

(unknown)

Attempts to prepare the ammono ketones analogous to the hydramides have resulted in the formation of ketisoketimines or other products [Moureu and Mignonac]. Although Thomae [*Archiv. Pharm.*, **243**, 373 (1905); *ibid.*, **244**, 641 (1906); *ibid.*, **246**, 373 (1908)] claims to have prepared an ammono ketone analogous to the hydramides by the action of ammonia on ethyl methyl ketone, his work has been questioned by Traube [*Ber.*, **41**, 777 (1908); *ibid.*, **42**, 3298 (1909)], who could not duplicate the results.

one if it takes place according to the equation $R_2C{=}O + NH_3 = R_2C{=}NH + H_2O$, the yields of ketimine should be increased by increasing the concentration of the ammonia as, for example, by the use of anhydrous liquid ammonia. As a matter of fact the writer has found that liquid ammonia ammonolyzes aromatic and aromatic-aliphatic ketones to the corresponding ketimine and water.

Removal of the water formed during the ammonolysis should further serve to increase the yield of the ketimine. Attempts to use metallic amides as dehydrating agents resulted in the formation of metallic salts of the ketones. Phosphoric anhydride in contact with liquid ammonia formed a sticky mass which was not active as a dehydrating agent. Calcium chloride also failed to exhibit dehydrating properties in liquid ammonia. Finally, it was found that aluminum chloride was an excellent dehydrating material which could be used in weakly acid solution, that is, in the presence of ammonium salts. By the use of this material in liquid ammonia solution, a number of the ketimines were prepared.

Experimental

Preparation of the Aluminum Chloride.—Aluminum chloride reacts so vigorously with ammonia that the reaction cannot be carried out in the soft glass reaction tubes usually employed in working with liquid ammonia. Accordingly the following procedure was adopted. A rapid stream of ammonia gas was passed over the surface of the aluminum chloride contained in a pyrex test-tube which was supported in a vertical position by means of an iron clamp. The heat of the reaction caused the aluminum salt to melt and as it did so the glass nozzle through which the ammonia was delivered was pushed down into the liquid in order to keep it stirred. When heat ceased to be evolved, the current of ammonia was stopped and the fluid melt poured into a nickel dish where it was allowed to solidify. As soon as it was cool enough to handle, it was pulverized in a mortar, then preserved in a tightly stoppered bottle for future use. When placed in liquid ammonia, the mixture forms a white flocculent mass which settles well.[4]

Ammonolysis of Acetophenone.—Acetophenone was heated with twice its volume of liquid ammonia in a sealed tube at 180° for four hours.[5] After cooling the ammonia was evaporated and the residue dissolved in ether. The ethereal solution was saturated with dry hydrogen chloride, when a white precipitate was obtained. This hydrochloride was filtered off, washed with ether, dissolved in chloroform and reprecipitated with ether. The white crystalline salt thus obtained was slightly hygroscopic, decomposing upon standing in contact with moist air.

Anal. Calcd. for $C_8H_{10}NCl$: Cl, 22.8. Found: Cl, 23.3.

The yield of the acetophenone-imine obtained in the above experiment amounted to 3% of the theoretical quantity. In order to increase this yield the experiment was repeated using a large excess of the aluminum chloride as a dehydrating agent. In this case a yield amounting to 30% of the theoretical was obtained.[6]

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[4] Although the composition of the compound obtained was not determined, it is probably a mixture of aluminum chloride, ammonium chloride, aluminum chloride with ammonia of crystallization and partly ammonolyzed aluminum chloride.

[5] For method of heating see Blair, THIS JOURNAL, **48**, 87 (1926).

[6] No evidence of the compounds reported by Thomae [*Arch. Pharm.*, **244,** 641 (1906)] and by Paternò and Maselli [*Gazz. chim. ital.*, **42,** I, 65 (1912)] was found.

Ammonolysis of Methyl *p*-Tolyl Ketone.—When methyl *p*-tolyl ketone was ammonolyzed by the method applied to acetophenone, a ketimine hydrochloride was obtained which was very unstable. The analysis of three different preparations showed too high a percentage of chlorine and of nitrogen.

Ammonolysis of Fenchone.—Fenchone was heated at 180° for four hours with four times its volume of anhydrous ammonia and an excess of aluminum chloride. After evaporation of the ammonia the residue was treated as described above for acetophenone, when a white crystalline precipitate of fenchone-imine was obtained. These crystals melted at 274–278° with slight darkening. The melting point of fenchone-imine hydrochloride previously recorded is 278°.[7]

Ammonolysis of Camphor.—Camphor imine was prepared by the method described above and isolated as the hydrochloride. Camphor imine hydrochloride separates from a chloroform–ether solution in long transparent crystals which grow rather slowly. This compound sublimes without decomposing and appears to be identical with the hydrochloride which Mahla and Tiemann obtained by treating camphor imine with hydrogen chloride.[8]

Anal. Calcd. for $C_{10}H_{18}NCl$: Cl, 18.9; N, 7.5. Found: Cl, 19.5, 19.6; N, 6.9.

Reduction of Camphor Imine to Bornylamine.—Camphor imine hydrochloride was suspended in ether, treated with an excess of ammonia and filtered from the precipitated ammonium chloride. The solution was then treated with metallic sodium and finally with alcohol. After the sodium had dissolved, the solution was diluted with water, the ether was evaporated and the residue neutralized with hydrochloric acid. The bornylamine, which is an ammono alcohol, was then precipitated as the picrate, which was recrystallized from water and alcohol. The purified compound melted with decomposition at 241.5° uncorr.[9]

Ammonolysis of Benzophenone.—Benzophenone-imine hydrochloride was prepared by the method used in the preparation of fenchone-imine hydrochloride. The small white crystals which were obtained sublime without decomposing. The yield was 20% of the theoretical.

Anal. Calcd. for $C_{13}H_{12}NCl$: Cl, 16.3; N, 6.4. Found: Cl, 16.4; N, 6.4.[10]

Ammonolysis of Benzil.—Liquid ammonia reacts very slowly with benzil at room temperature forming benzamide and imabenzil, the latter being insoluble in liquid ammonia. Upon heating benzil with liquid ammonia at 200° for two hours, 40% of the ketone is converted into lophine, triphenylimidazole, which is only slightly soluble

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[7] Mahla [*Ber.*, **34**, 3777 (1901)] prepared fenchone-imine by the action of nitrous acid on fenchone-oxime.

[8] Mahla and Tiemann, *Ber.*, **29**, 2808 (1896).

[9] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1916**, Vol. II, p. 116.

[10] Benzophenone-imine was first prepared by Hantzsch and Kraft [*Ber.*, **24**, 3517 (1891)], who ammonolyzed benzophenone chloride with urethan, a substituted ammonia. Although Pauly [*Ann.*, **187**, 196 (1877)] was unable to ammonolyze benzophenone with ammonia, Thomae [*Arch. Pharm.*, **243**, 395 (1905)] claims to have prepared benzophenone-imine by the direct ammonolysis of benzophenone with alcoholic ammonia. Later Moureu and Mignonac [*Compt. rend.*, **156**, 1801 (1913)] prepared benzophenone-imine by the action of Grignard reagent on acetonitrile, a reaction which is analogous to the addition of Grignard reagent to an acid anhydride. Cornell [THIS JOURNAL, **50**, 3314 (1928)] and Smith [unpublished work] have used liquid ammonia to decompose the Grignard addition compound.

in liquid ammonia. These results are similar to those obtained by other workers who used alcoholic ammonia.[11]

The writer is greatly indebted to Dr. E. C. Franklin, who constantly expedited the experimental work with his erudite suggestions.

Summary

A method of ammonolyzing ketones has been developed and applied. The formation of a number of ketimines, which are ketones of the ammonia system as developed by Franklin, is described.

A compound of ammonia and aluminum chloride has been found to be an excellent dehydrating agent in liquid ammonia.

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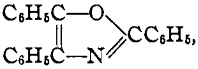
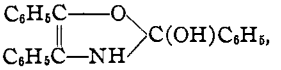
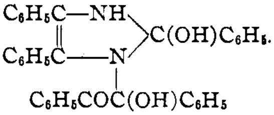
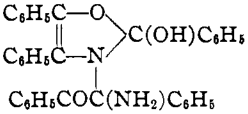
[11] Laurent, *J. prakt. Chem.*, **35**, 416 (1845); Japp and Wynne, *J. Chem. Soc.*, **49**, 477 (1886); Henius, *Ann.*, **228**, 339 (1885); Pinner, *Ber.*, **35**, 4138 (1902).

The formula for benzilam given by Japp and Henius is , that for benzilimide is , while Pinner has suggested the following formula for imabenzil, . However, Henius has shown that imabenzil is easily converted into benzilimide and benzilam, indicating that an oxygen atom may be contained in the ring. Accordingly Pinner's formula might be modified to one of the following



or