[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

METALLIC SALTS OF KETONES

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RECEIVED MAY 19, 1930 PUBLISHED AUGUST 5, 1930

Upon attempting to use metallic amides as dehydrating agents to promote the reaction between ketones and liquid ammonia, the writer found that metallic salts of the ketones were formed.[1] A search of the literature then revealed that such salts had been prepared by the action of ketones on metallic amides in the presence of indifferent solvents,[2] and by the action of sodium on the ketones.[3]

Because of the very weak acid properties of the ketones, the use of the indifferent solvents as a liquid medium in the preparation of their salts has been requisite. In general such liquids are poor solvents for metallic salts, so that much difficulty is entailed in preparing and recrystallizing the latter. The poor ionizing properties of the common indifferent solvents also causes the reaction between the ketone and the metallic amide to proceed very slowly.

Since liquid ammonia possesses unique ionizing, solvolyzing and solvent properties which make it an advantageous medium for preparing salts of very weak acids,[4] it was tested as a solvent for the salts of ketones and found to serve admirably. The salts prepared by its use are described below.

Methods

All salts were prepared and purified in liquid ammonia solution. The methods of handling the ammonia were essentially the same as those described by Franklin.[5]

The salts were formed in two-legged tubes by pouring a solution of the ketone over an excess of the metallic amide. After the reaction had run to completion the solution was decanted from excess amide and concentrated until crystals separated. The crystals were then washed with liquid ammonia and dried *in vacuum*. The tube was subsequently opened by scratching with a file and breaking with a drop of hot glass. The end of the tube containing the crystals was stoppered and the weight of the sample deter-

[1] Strain, THIS JOURNAL, **52**, 820 (1930).

[2] Merling, Chrzesciuski and Pfeffer, U. S. Patent 1,169,341, January, 1925; *C. A.*, **10**, 952 (1916).

[3] Haller, "Dissertation," Nancy, **1879**, p. 41. Haller and Bauer [*Ann. chim. phys.*, [8] **28**, 373 (1913); [8] **29**, 313 (1913)] have shown that many ketones are alkylated when treated with sodium amide and an alkyl halide, a reaction which indicates the intermediate formation of a salt of the ketone.

[4] Franklin, *J. Phys. Chem.*, **24**, 81 (1920); Strain, THIS JOURNAL, **49**, 1995 (1927); Cornell, *ibid.*, **50**, 3311 (1928).

[5] Franklin, *J. Phys. Chem.*, **15**, 513 (1911); Ref. 4.

mined by weighing the stoppered tube before and after removing a portion of the salt to a platinum crucible. Sodium and potassium were determined as sulfates, calcium as the oxide.

All salts are stable to 60° either *in vacuum* or in an atmosphere of ammonia. Exposed to the air, however, they undergo a very vigorous decomposition. They are rapidly hydrolyzed by water to the ketone and the metallic hydroxide.

TABLE I

SALTS OF KETONES

Ketone	Metal	Formula	Cryst. form	Color	Soly.	—Metal, %— Calcd.	Found
Acetone[a]	Na	C_3H_5ONa	.....	None	Very	28.8	29.2
	Ca	$(C_3H_5O)_2Ca$	.....	None	Very	26.0	26.3
Methylpropyl	Na	C_5H_9ONa	None	None	Very	21.3	24.5
Acetophenone	Na	C_8H_7ONa	.....	None	Very	16.2	16.9
	Ca	$(C_8H_7O)_2Ca$	*Prisms*	*None*	Sol.	14.4	14.2
Methyl *p*-tolyl	Na	C_9H_9ONa	None	...	Very	14.8	15.4
Camphor	Na	$C_{10}H_{15}ONa$	....	None	Med.	13.2	13.8
Fenchone	Na	$C_{10}H_{15}ONa.XNH_3$	Distorted cubes	None	Sl.	..	..
		$C_{10}H_{15}ONa$	Amorphous	White	...	13.2	12.6
Benzophenone[b]	Na	$C_{13}H_{10}ONaNH_2$	Short needles	None	Sol.	10.4	11.0
	K	$C_{13}H_{10}ONK_3$	Flakes	None	Sl.	37.4	39.8
							40.8
				Nitrogen, calcd.		4.5	6.0

[a] For references relating to the preparation of metallic salts of acetone in indifferent solvents see Bacon and Freer, *C. A.*, **1**, 1695 (1906); Bayer and Company, *ibid.*, **10**, 2615 (1916).

[b] Haller and Bauer [*Ann. chim. phys.*, [8] **16**, 146 (1909)] report the formation of a compound having the formula $(C_6H_5)_2C(NH_2)ONa$ which they analyzed and found to contain 10.6–10.9% sodium. These values are in rather good agreement with the theoretical value, which is 10.4%, rather than 11.7% as given by Haller and Bauer. The potassium salt of benzophenone represents a rather unusual compound. For a time it appeared that this salt might be dipotassium benzamide, which should contain 39.7% potassium [Pauline Lucas, *ibid.*, [8] **17**, 127 (1909)]. However, benzamide does not form a dipotassium salt [Ruth Fulton, "Thesis," Stanford University (1926)]. This salt is also quite different from the dipotassium derivative of benzophenone prepared by the action of potassium on benzophenone [Wooster, THIS JOURNAL, **50**, 1388 (1928); *ibid.*, **51**, 1856 (1929)].

Summary

A number of metallic salts of ketones have been prepared by the action of metallic amides on ketones in liquid ammonia.

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