The Reactions of Silicomolybdic Acid with Organic Compounds[1]

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For many years the analytical and inorganic chemists have been seeking specific reagents to identify metallic ions. At the same time, the organic chemist has been interested in finding compounds that would be useful for spotting different types of functional groups commonly encountered in organic compounds. A typical example of such a reagent is ferric chloride, which has found wide use with phenols.

For several years we have been testing various compounds in an effort to find reagents that would be specific for metallic ions as well as organic functional groups. In the course of our investigation it was found that silicomolybdic acid (1), $H_4SiMo_{12}O_{40}.xH_2O$, would produce a dark blue mixture in the presence of aliphatic aldehydes, but would not give the same test with aromatic aldehydes. Further investigation indicated that only aldehydes that contain a hydrogen atom on the alpha carbon atom would give a positive test. On the basis of this work a more thorough study was undertaken of the reaction of silicomolybdic acid with various organic compounds containing different functional groups. Altogether the reagent has been tried with a one-hundred and forty-five organic compounds. Table 1 shows the aldehydes that have been tested.

TABLE I

Aldehydes

—	Formaldehyde	—	Benzaldehyde
+	Acetaldehyde	—	m-Nitrobenzaldehyde
+	Phenylacetaldehyde	—	p-Nitrobenzaldehyde
+	Propionaldehyde	—	2,4-Dichlorobenzaldehyde
+	n-Butyraldehyde	—	p-Hydroxybenzaldehyde
+	Isobutyraldehyde	—	m-Hydroxybenzaldehyde
+	α-Ethylbutyraldehyde	—	o-Methoxybenzaldehyde
+	n-Valeraldehyde	—	p-Methoxybenzaldehyde
+	Isovaleraldehyde	—	2,4-Dihydroxybenzaldehyde
+	α-Ethylcaproaldehyde	—	2,4-Diethoxybenzaldehyde
+	n-Heptaldehyde	—	2,4-Dimethoxybenzaldehyde
+	Crotonaldehyde	—	2,3-Dimethoxybenzaldehyde
+	Acrolein	—	3,4-Diethoxybenzaldehyde
+	Aldol	—	p-Dimethylaminobenzaldehyde
—	Chloral hydrate	—	Salicylaldehyde
—	α-Amylcinnamaldehyde	—	Cinnamaldehyde

In Table I, plus signs indicates positive results and negative signs indicate negative results. A negative result was regarded as any color

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other than dark blue throughout the mixture. In some cases yellow, green, brown, or pale blue colors developed, or a small amount of dark blue formed in the bottom layer of the test tube. All these results were regarded as negative tests.

According to the alpha hydrogen rule one would expect cinnamaldehyde to give a positive test. However, the results were negative. An explanation of this may be that cinnamaldehyde being a vinylog of benzaldehyde, behaves in the same way benzaldehyde does toward silicomolybdic acid.

Since monosaccharides are generally regarded as potential aldehydes, several of the more common pentoses and hexoses were tested, and found to give negative results. Some disaccharides were also tested and they failed to give positive results. Table II contains a list of the carbohydrates that were tested.

TABLE II

Monosaccharides	Disaccharides
— Arabinose	— Sucrose
— D(—) Ribose	— Lactose
— D(+) Xylose	— Maltose
— D(+) Glucose	
— D(+) Mannose	
— D(+) Galactose	
— L(+) Fructose	
— L(—) Sorbose	

Most ketones also contain a carbonyl group with hydrogen atoms on the alpha carbon atom, and therefore, one might expect them to behave similar to aldehydes toward silicomolybdic acid. However, all of the ketones which were tested gave negative results. See Table III.

TABLE III

Ketones

— Acetone	— Acetylacetone
— Methyl ethyl ketone	— Diacetyl
— Diethyl ketone	— Acetophenone
— Methyl isobutyl ketone	— Benzophenone
— Methyl pentyl ketone	— Benzalacetophenone
— Cyclopentanone	— Benzalacetone
— Cyclohexanone	— Acetoacetanilide

A large number of other compounds were tested among the hydrocarbons, alcohols, esters, ethers, acids, nitriles, phenols, and amines. The results of these tests are shown in Table IV.

TABLE IV

Aliphatic Hydrocarbons

— n-Hexane
— n-Heptane
— 1-Pentene
— 2-Pentene
— Cyclohexene

Aromatic Hydrocarbons

— Benzene
— Toluene
— o-Xylene
— p-Xylene
— Naphthalene
— Anthracene

Alcohols

— Methyl alcohol
— Ethyl alcohol
— n-Propyl alcohol
— Isopropyl alcohol
— n-Butyl alcohol
— Isobutyl alcohol
— sec-Butyl alcohol
— tert-Butyl alcohol
— n-Amyl alcohol
— Allyl alcohol
— Cyclohexyl alcohol
— Ethylene glycol
— Glycerol
— Cinnamyl alcohol
— Benzyl alcohol

Ethers

— Diethyl ether
— Butyl cellosolve
— Dioxane
— Anisole

Esters

— Ethyl acetate
— Ethyl malonate
— Ethyl acetoacetate
— Ethyl benzoate
— Ethyl phthalate
— Methyl salicylate

Acids

— Acetic acid
— Propionic acid
— Valeric acid
— Lactic acid
— Citric acid
— Benzoic acid
— Pyruvic acid
— Cinnamic acid

Nitriles

— Acetonitrile
— n-Butyronitrile
— n-Capronitrile
— Acrylonitrile
— Benzonitrile
— Benzoylacetonitrile
— Cyanoacetic acid

Phenols

— Phenol
— β-Naphthol
— p-Aminophenol (green)
— m-Aminophenol (brown)
— c-Aminophenol (brown)
— Picric acid (orange)

Aliphatic Amines

— Isopropylamine
— α -Phenylethylamine
— β -Phenylethylamine
— Ethylenediamine

Aromatic Amines

— Aniline
— Benzylamine
— Diphenylamine
— m-Nitroaniline
— N,N-Dimethylaniline

As can be seen from all the data listed in the tables, the test with silicomolybdic acid appears to be specific for aldehydes with an hydrogen atom on the alpha carbon atom.

TABLE V

Aldehydes	Phenols
+ Glyoxal	+ α-Naphthol
+ Furfuraldehyde	+ Hydroquinone
+ Hydroxypyruvaldehyde	+ Resorcinol
Amines	+ Phloroglucinol
+ Pyrrole	+ Gallic acid
+ N-Benzylpyrrole	
+ o-Phenylenediamine	
+ p-Phenylenediamine	
+ N-Methyl-p-aminophenol	

Table V, contains a list of other compounds that were tested and which gave positive results. It should be noted that none of the aldehydes possess an alpha hydrogen. These anomalous results may be attributed to the presence of aldehydes with an alpha hydrogen atom on them, as impurities in the chemical compound that was tested. For example, on several occasions positive tests were obtained, but when a pure compound was tested no color was obtained. Cinnamaldehyde was such a case. When a test was made on cinnamaldehyde which came from a bottle that had been used for several years and in which a deposit of cinnamic acid had formed, a positive test was produced. However, pure cinnamaldehyde did not give the test, nor did a mixture of pure cinnamaldehyde and cinnamic acid.
A possible explanation is that the positive test might have occurred due to the presence of acetaldehyde which might have been formed by the hydrolysis of the double bond in cinnamaldehyde.

Molecules that are easily oxidized, such as, the polyphenolic compounds and the N-substituted aminophenols, give a positive test. At first it might seem that these compounds would interfere with the test for the aldehydes. However, this need not be the case if one follows the solubility procedures outlines by either Shriner and Fuson or McElvain (2, 3). In these solubility schemes, amines will be separated in the acid soluble portion, and phenols in the base soluble portion. Other nitrogen containing compounds will fall in a miscellaneous class. The aldehydes will be found either in the water soluble portion or in the neutral portion that is not soluble in water. None of the compounds tested thus far that gave anomalous results fall in the latter two groups and thus do not interfere with the test for aliphatic aldehydes with an alpha hydrogen atom.

The investigation was extended to other inorganic compounds such as, silicotungstic acid, molybdic acid, and phosphomolybdic acid. Under conditions that were tried neither silicotungstic acid nor molybdic acid gave a color with the aldehydes that were tested. However, phosphomolybdic acid gave colored results similar to silicomolybdic acid with the compounds that were tested. The authors are currently investigating the behavior of phosphomolybdic acid as a possible specific reagent for detecting organic functional groups. Likewise an investigation is being conducted to determine the possible use of these reagents for the quantitative determination of aliphatic aldehydes.

The authors wish to emphasize that this is a preliminary report and work is in progress investigating more complex organic groups and molecules. Likewise, the upper molecular weight of the test for aliphatic aldehydes needs to be determined, and more aliphatic aldehydes with no hydrogen atom on the alpha carbon atom should be examined.

Procedure

Add 0.1 ml of the compound to be tested to 5 ml of 95 percent ethanol. If a solid compound is tested use ten milligrams. Add 0.5 ml of a 0.1 molar solution or suspension of silicomolybdic acid to the mixture and shake fifteen seconds. Then add 0.5 ml of a solution four molar to sodium hydroxide and two molar to sodium carbonate. The appearance of a dark blue color throughout the mixture indicates a positive test.

Summary

1. Silicomolybdic acid has been found to be almost a specific reagent to detect aliphatic aldehydes with a hydrogen on the alpha carbon atom.
2. Silicomolybdic acid may be used to distinguish between aromatic and aliphatic aldehydes.
3. Aliphatic aldehydes with an alpha hydrogen atom may be detected in the presence of ketones by the use of silicomolybdic acid.
4. Since silicomolybdic acid is essentially specific for aliphatic aldehydes it may be useful to identify such aldehydes in naturally occurring products, in other compounds in the laboratory, and as impurities in compounds prepared from aldehydes or those that might form aldehydes as a by-product of a reaction.

Literature Cited

1. NORTH, E. O. 1939. Inorganic Synthesis. McGraw-Hill Co., First Ed., p. 129.
2. SHRINER, R. L., and R. C. FUSON. 1940. Identification of Organic Compounds. John Wiley and Sons, Inc. Second Ed., p. 4.
3. MCELVAIN, S. M. 1945. The Characterization of Organic Compounds, Macmillan and Co.