

bulb, 351.4 cc. Calcd. for  $H_2$ : 2.0. Found: 3.1, 3.9. *Total vol. of gas.* Subs., 1.086, 1.029; Na, 0.096, 0.091; *P*, 200, 212 mm.; *T*, 25°, 27°; vol. of system, 391 cc.; vol. of pure H at N.T.P., corr. for  $NH_3$  content, 87.0, 86.4 cc. Gram atoms of  $H_2$  per mole of  $(C_6H_5)_3SiH$ , 1.8, 1.9.

### Summary

1. The constitution of triphenylsilicane, melting at 36°, has been established.

2. The reaction between triphenylsilicane and sodium in liquid ammonia has been studied. The chief product of the reaction was found to be di-triphenylsilicon-imine,  $[(C_6H_5)_3Si]_2NH$ .

PROVIDENCE, RHODE ISLAND

---

[CONTRIBUTION FROM THE DENVER STATION, FOOD, DRUG AND INSECTICIDE  
ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

## MONOBROMOGUAIACOL CARBONATE. ESTIMATION OF GUAIACOL CARBONATE

BY LEWIS H. CHERNOFF

RECEIVED MAY 1, 1929

PUBLISHED OCTOBER 5, 1929

As far as the writer is aware there are only two published methods for the estimation of guaiacol carbonate. One method<sup>1</sup> depends on the solubility of the carbonate in ether and its use is therefore limited to mixtures which do not contain other ether-soluble substances. In the other<sup>2</sup> the substance is saponified with alcoholic potassium hydroxide, acidified and after the addition of sodium chloride the volume of guaiacol is read.

The method herein described is more specific and depends on the conversion of guaiacol carbonate into a bromine derivative insoluble in 50% methyl alcohol.

When bromine is added to a solution of guaiacol carbonate in methyl alcohol, large needle-like crystals begin to separate out almost immediately. The compound is reasonably pure and after recrystallization from hot 95% ethyl alcohol melts sharply to an oil at 178°. It is easily soluble in chloroform, ether, benzene and hot methyl and ethyl alcohols, but less easily soluble in the cold alcohols. In water and petroleum ether it is insoluble.

A bromine determination by the Pringsheim method<sup>3</sup> slightly modified indicates the compound to be a monobromo guaiacol carbonate. This is apparently a new compound, as it does not seem to be described in the literature.

<sup>1</sup> Abstracted in *Quart. J. Pharm.*, **1**, 432 (1928); *Apoth. Ztg.*, **43**, 198 (1928).

<sup>2</sup> A. Fernan, *Z. Oesterr. Apoth. Vr.*, **49**, 165 (1911); *C. A.*, **5**, 3324 (1911).

<sup>3</sup> Scott, "Standard Methods of Analysis," D. Van Nostrand Co., Inc., New York, 1917, 2d ed., revised, p. 122; *Chem. News*, **91**, 215, 2372 (1905). The mixture of substance with sodium peroxide was heated slowly in a nickel crucible until melted. The contents was then allowed to cool and the whole plunged into water.

*Anal.* Subs., 0.2 g.: AgBr, 0.1763. Calcd. for  $(\text{BrC}_6\text{H}_2\text{OCH}_3)_2\text{O}_2\text{CO}$ : Br, 37.07. Found: Br, 37.50.

### Method

To 0.1–0.5 g. of guaiacol carbonate in a 100-cc. Erlenmeyer flask add 10–20 cc. of methyl alcohol. Heat on the steam-bath until all of the substance is dissolved. Remove from the bath while hot, add about 1 cc. of bromine and let stand for ten minutes, shaking occasionally to promote crystallization. Add an equal volume of water and allow to stand for ten minutes longer. Filter through asbestos in a weighed Gooch crucible, wash with 50% methyl alcohol, dry for about an hour at the temperature of boiling water and weigh. Multiply the weight of the bromine derivative by the conversion factor 0.6343 to obtain the weight of guaiacol carbonate.

The bromine derivative is somewhat soluble in methyl alcohol and the addition of water is necessary to precipitate it completely. The following table shows the results obtained with pure guaiacol carbonate.

TABLE I  
RESULTS WITH PURE GUAIACOL CARBONATE

Subs., g.	Bromine deriv., g.	Equiv. guaiacol carbonate, g.	Error, %
0.5	0.7788	0.4939	1.2
.1	.1567	.0994	0.6
.1	.1575	.0999	.1
.01	.0158	.0100	.0

When only one-fourth volume of water is added, the error becomes slightly larger, as is shown in Table II.

TABLE II  
ERROR WITH LESS WATER

Subs., g.	Bromine deriv., g.	Equiv. guaiacol carbonate, g.	Error, %
0.5	0.7586	0.4812	3.8
.1	.1533	.0972	2.8
.1	.1557	.0988	1.2

### Mixtures

In mixtures with the usual excipients such as starch, sugar and the gums acacia and tragacanth, a preliminary separation by the use of proper solvents may be made. Chloroform, in which the carbonate is easily soluble, is useful.

Mix 0.5 to 0.1 g. of powdered material with 10 cc. of chloroform, heat to boiling and filter through a small paper into an evaporating dish. Wash thoroughly with chloroform and evaporate the solution on the steam-bath. Dissolve the residue in hot methyl alcohol and brominate as above.

The results shown in Table III were obtained on three different mixtures whose compositions were unknown to the writer at the time of analysis. Later their compositions were given for comparison.

TABLE III  
RESULTS ON UNKNOWN MIXTURES

Mixture	Composition, %	Guaiacol carbonate found, %
1	Guaiacol carbonate, 31.5; sucrose, 0.5; starch, 68.0	29.38, 30.64
2	Guaiacol carbonate, 51.5; sucrose, 9.5; acacia, 1.0; starch, 38.0	49.16, 49.76
3	Guaiacol carbonate, 63.7; tragacanth, 0.3; starch, 36.0	63.5, 63.89

A sample of commercial 5-grain guaiacol carbonate tablets was prepared by pulverizing twenty tablets, the average weight of each being 0.3865 g. or 5.96 grains. Three-tenths gram samples were analyzed according to the method for mixtures, with the check results 75.53 and 75.56%. The average content, therefore, was 4.50 grains instead of the declared 5 grains.

### Summary

A new method for the estimation of guaiacol carbonate, depending on the conversion of guaiacol carbonate into a monobromo derivative, and a new compound, monobromo guaiacol carbonate, are described.

Acknowledgement is made to L. E. Warren of the Food, Drug and Insecticide Administration for submitting the problem and furnishing the "unknowns."

DENVER, COLORADO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]  
**NEW DERIVATIVES OF CREATININE AND DIKETOPIPERAZINE<sup>1,2</sup>**

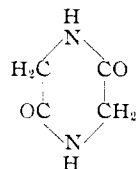
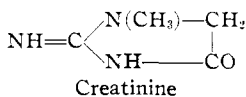
BY L. R. RICHARDSON AND CLAUDE E. WELCH WITH S. CALVERT

RECEIVED MAY 25, 1929

PUBLISHED OCTOBER 5, 1929

Creatinine, since it is excreted by the animal body, and diketopiperazine, because recent research has indicated that it is an integral part of the protein molecule, are both of great physiological importance. Extensive investigations of the physiological nature of creatinine have been completed but the known chemical reactions of both compounds are comparatively few in number.

A consideration of the formulas of these substances shows that both contain methylene groups



Diketopiperazine (keto form)

<sup>1</sup> An abstract of the theses submitted by L. R. Richardson and Claude E. Welch in partial fulfillment of the requirements for the degree of Master of Arts in Chemistry at the University of Missouri.

<sup>2</sup> Revised paper; original manuscript received August 6, 1928.