[Contribution from the Chemical Laboratory of the University of Colorado]

THE ACTION OF GUANIDINE CARBONATE AND OF BENZAMIDINE HYDROCHLORIDE UPON GLYOXAL SODIUM BISULFITE

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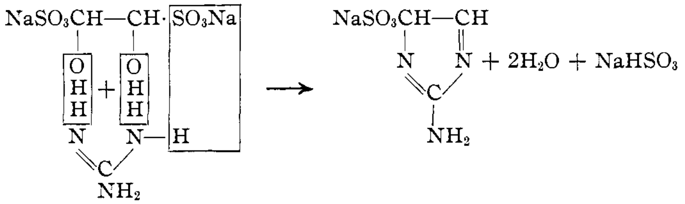
Very little has been published upon the reaction of guanidine or of benzamidine salts upon dialdehydes and diketones and, so far as we know, nothing upon their reactions with glyoxal sodium bisulfite. Wense[1] obtained mono- and diguanylbenzil and diguanylphenanthrenequinone from guanidine carbonate with benzil and phenanthrenequinone, respectively. By the action of benzamidine hydrochloride upon diacetyl, Diels and Schleich[2] obtained a very interesting addition product which, from its properties, seems to be a dihydroglyoxaline derivative.

This paper will describe compounds obtained by condensing guanidine carbonate and benzamidine hydrochloride, respectively, with glyoxal sodium bisulfite.

Guanidine carbonate reacts with glyoxal sodium bisulfite yielding the sodium salt of an aminosulfonic acid of a tautomeric form of glyoxaline, according to the following reaction



That the compound has the structure assigned to it is shown by the analysis, by the absence of a NH group (Liebermann's reaction), and by the fact that the NH_2 group may be replaced by OH by treatment with nitrous acid, yielding the corresponding hydroxy acid. Acidifying the salt or carrying out the reaction in acid solution would be expected to give the free acid. This, however, is not the case, since, as fast as the acid group is liberated, it reacts with the amino group, yielding the inner salt A, as is shown by the fact that the resulting compound is neutral. Boiling this compound with sodium hydroxide yields the original sodium salt. Nitrous acid reacts with the inner ammonium salt giving the corresponding hydroxy acid, B.

Benzamidine hydrochloride reacts in a similar manner with glyoxal sodium bisulfite, in this case forming the sulfonic acid of a tautomeric form of phenylglyoxaline, C.

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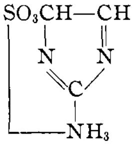
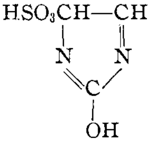
[1] Wense, *Ber.*, **19**, 762 (1886).

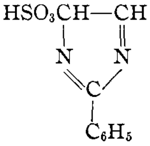
[2] Diels and Scheich, *ibid.*, **49**, 1713 (1916).



A



B



C

At 100° the compound, if slightly impure, loses sulfur dioxide and water, changing to a dark red resinous solid. Even at 80° the decomposition takes place slowly and at the end of a week the sample lost 26.3% of its weight. After raising the temperature to 100°, it lost 33.8%. The theoretical loss for sulfur dioxide in the above compound is 26.45% and for sulfur dioxide and water is 33.9%. If the compound is pure, it is stable, the crystals remaining unchanged apparently indefinitely.

Experimental

Sodium Salt of 2,4-Aminoglyoxalinesulfonic Acid.—Guanidine carbonate and glyoxal sodium bisulfite were brought together in water solution and boiled. Carbon dioxide was given off and, on evaporating the solution, colorless crystals were obtained. There was some decomposition during the concentration, the solution becoming light brown. The crystals were recrystallized from hot water, yielding colorless transparent prisms, which on drying became opaque. The sample for analysis was dried at 100° and melted at 260–263°.

Anal. Calcd. for $C_3H_4N_3NaSO_3$: C, 19.44; H, 2.18; N, 22.70; S, 17.32; Na, 12.42. Found: C, 19.22; H, 2.20; N, 22.41; S, 17.68; Na, 12.51.

The mother liquor was evaporated and allowed to cool, whereupon crystals of acid sodium sulfite separated out.

Inner Ammonium Salt of Aminoglyoxalinesulfonic Acid.—This compound is formed when the above sodium salt is acidified with hydrochloric acid or when water solutions of equimolecular proportions of guanidine carbonate and glyoxal sodium bisulfite are mixed, acidified with hydrochloric acid, concentrated and allowed to crystallize, whereupon colorless crystals of the inner salt are obtained. Recrystallized from hot water, they melt at 172–174°.

Anal. Calcd. for $C_3H_4N_3SO_3H$: C, 23.36; H, 2.61; N, 27.27; S, 20.80. Found: C, 23.33; H, 3.01; N, 27.02; S, 21.11.

2-Hydroxy-4-glyoxalinesulfonic Acid.—To an ice-cold water solution of the inner ammonium salt, acid with hydrochloric acid, cold sodium nitrite solution was added and allowed to stand. On concentrating the solution, colorless crystals were obtained which, recrystallized from hot water, melted at 225°.

Anal. Calcd. for $C_3H_3N_2SO_4H$: N, 17.07. Found: N, 17.10.

2-Phenyl-4-glyoxalinesulfonic Acid.—Molecular quantities of benzamidine hydrochloride and glyoxal sodium bisulfite were dissolved in warm water, mixed and concentrated on the water-bath. On cooling, a colorless crystalline compound was obtained which, recrystallized from hot water, melted at 109°. When impure, the crystals gradually decompose, but the pure compound is stable.

Anal. Calcd. for $C_9H_7N_2SO_3H$: C, 44.62; H, 4.13; N, 11.57; S, 13.22. Found: C, 44.74; H, 4.06; N, 11.53; S, 13.08.

Summary

1. The inner ammonium salt of 2-amino-4-glyoxalinesulfonic acid has been prepared. On boiling with sodium hydroxide, the sodium salt of the acid is obtained.

2. 2-Hydroxy-4-glyoxalinesulfonic acid has been prepared.

3. 2-Phenyl-4-glyoxalinesulfonic acid has been prepared.

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NORMAL VALEROLACTONE. II. ITS VAPOR PRESSURE

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During the course of a study of the chemical and physical properties of *n*-valerolactone under way in this Laboratory, it became desirable to verify the statement that this compound distils without decomposition[1] at 206–207°. A determination of its vapor pressure, which hitherto has not been reported, seemed to afford the most direct method of approach in the attack on this problem.

Experimental Procedure

The *n*-valerolactone used in this study was prepared by the reduction of levulinic acid as described by one of us.[2] That which was used for experimentation was dried over anhydrous sodium sulfate and redistilled, the fraction boiling at 125.3 ± 0.2° (68 mm.) serving for the vapor pressure measurements.

Vapor pressure measurements were made over the temperature range 69 to 203.4° by the dynamic method of Ramsay and Young[3] and the static method described by Smith and Menzies.[4] In both methods pressures were read directly from a manometer with the aid of lenses. They are accurate to ±0.2 mm. The necessity of making stem corrections was avoided in the dynamic method[3] by suspending the thermometer in the vapor pressure flask. All observed thermometer readings in the static method[4] were corrected for stem exposure. Two series of measurements were made by each method.

It was found that the vapor pressure curve as plotted in the usual manner from the data obtained by the dynamic method[3] of measurement can be expressed by the empirical equation $\log P = -2540.44/T + 8.2059$. Similarly, the corresponding expression for the data obtained by the static

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[1] Messerschmidt, *Ann.*, **208**, 97 (1881).

[2] Schuette and Sah, THIS JOURNAL, **48**, 3163 (1926).

[3] Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

[4] Smith and Menzies, THIS JOURNAL, **32**, 1412 (1910).