

# SCIENTIFIC SECTION

## PREPARATION OF CARSTANJEN'S COMPOUND.\*

BY A. A. HARWOOD.

Any one who has had experience in making this compound may have come to the conclusion that its successful preparation is a matter of chance. Carstanjen himself did not give specific directions therefor. The difficulty may first of all be attributed to a more or less oxidized sulphite. It has also been attributed to an excess of caustic alkali formed in the course of the reaction. This, as already pointed out by Carstanjen, acts on the resulting compound causing it to be oxidized as well as hydrolyzed.

I. After a number of failures with commercial sulphites, even from sealed bottles, it was decided to prepare the sulphite fresh. One hundred grams of potassium hydroxide were dissolved in 100 cc. of water and the solution was saturated with sulphur dioxide. To the acid sulphite solution thus obtained, an equal amount of KOH was added to convert the acid salt into the normal sulphite. To 20 cc. of this solution, transferred to an Erlenmeyer flask, and heated to 60°, a small amount of thymoquinone was added, the mixture shaken until the thymoquinone had dissolved forming a yellow solution. The reaction mixture was heated to 85° and thymoquinone added in small amounts, shaking the mixture after each addition until an excess had been added as shown by an oily layer on the surface. During the entire process SO<sub>2</sub> gas was passed into the neck of the flask so as to replace the air by this gas. Upon cooling the sulphone crystallized out and was separated by filtration and dried in a vacuum desiccator. It intumescenced when heated and gave the red color reaction in alkaline solution as does Carstanjen's compound. When repeated, equally successful results were obtained. In one attempt, however, when too much thymoquinone was added at a time, a dark crystalline mass resulted, presumably thymoquinhydrone. Apparently part of the thymoquinone had been reduced to hydrothymoquinone by the SO<sub>2</sub> before it had time to react with the dissolved sulphite and the reduction product united with unreduced thymoquinone to quinhydrone.

II. As difficulty had been experienced in trying to prevent oxidation during the preparation of Carstanjen's compound by introducing CO<sub>2</sub> to exclude the air or with SO<sub>2</sub> to prevent oxidation, a new means of attack had to be sought. During the hydrolysis of potassium sulphite to the acid sulphite, potassium hydroxide is formed. This reacts with the potassium sulphite thymoquinone compound producing the labile trihydroxy cymene which readily oxidizes to, probably, monohydroxythymoquinone. To prevent the KOH from reacting, an equimolecular amount of potassium acid carbonate was added to the aqueous solution of potassium sulphite. The solution was then heated to 80° C. on the water-bath and thymoquinone added in small amounts. Toward the end of the process, the solution became quite dark and SO<sub>2</sub> gas was passed in when partial decoloration took place. The solution was placed in an ice-bath and allowed to cool whereupon the Carstan-

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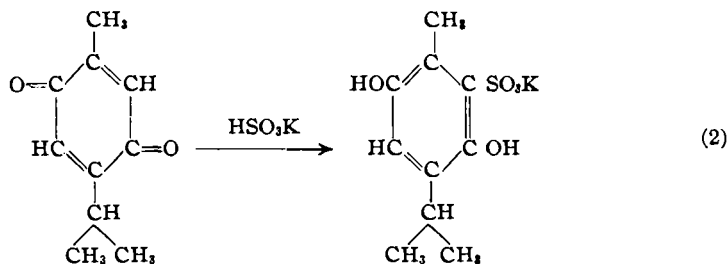
\* Presented to the Scientific Section. Part of a thesis presented as one of the requirements for the doctor's degree, University of Wisconsin.

jen compound crystallized out. The  $\text{SO}_2$  gas does not seem to reduce any excess thymoquinone as long as an excess of potassium acid carbonate is present.

III. Two attempts were made to prepare Carstanjen's compound with the aid of potassium acid sulphite instead of normal potassium sulphite. As soon as the solution of potassium acid sulphite was heated, an odor of  $\text{SO}_2$  was perceptible and, upon addition of thymoquinone, reduction to thymoquinhydrone took place later proceeding to hydrothymoquinone.

*The Sodium Analogue of Carstanjen's Compound.*—Previous attempts to prepare the sodium analogue to Carstanjen's compound resulted in the formation of tarry masses. Renewed attempts in this direction made with  $\text{Na}_2\text{SO}_3$  were no more successful. However, when acid sodium sulphite was used, a yellow solution without tar formation resulted. Inasmuch as no crystals separated, even upon cooling, the solution was evaporated and the residue crystallized from hot alcohol. White, needle-shaped crystals were thus obtained which were very soluble in water. With alkali the solution gave a red color. Upon ignition 32 p.c. of ash were obtained whereas  $\text{C}_{10}\text{H}_{13}\text{SO}_3\text{Na}$  should yield 27 p.c.  $\text{Na}_2\text{SO}_4$ .

*Rate of Hydrolysis of  $M'_2\text{SO}_3$  Induced by Thymoquinone.*—The reactions involved in the formation of Carstanjen's compound have been explained by the following equations and formulas:<sup>1</sup>



It has already been pointed out that the KOH not only causes the sulphone to be hydrolyzed but, as Carstanjen states, the alkaline solution absorbs oxygen and the triatomic phenol formed by the hydrolysis is oxidized. Subsequent changes need not here be considered, but it may be well to remind that tarry products have frequently resulted, more particularly when  $\text{Na}_2\text{SO}_3$  was substituted for  $\text{K}_2\text{SO}_3$ .

Hewitt<sup>2</sup> has tried to determine the amount of KOH set free by the repeated addition of one-tenth moles of thymoquinone. The color interfered with ordinary titration using indicators. It occurred that the problem might be solved by neutralizing the alkali as formed after each addition of thymoquinone. Better still, it might be even more expedient to determine the reduction in acidity of sodium acid sulphite after each addition of thymoquinone. For the sake of comparison, parallel experiments were made with  $\text{Na}_2\text{SO}_3$  and  $\text{NaHSO}_3$ . One-tenth gram molecule of thymoquinone was used in the first experiment, two-tenth Gm. molecule in the second, etc. The  $\text{Na}_2\text{SO}_3$  experiments gave the usual tarry mass upon evaporaton

<sup>1</sup> Carstanjen, *J. prakt. Chem.*, 123, page 478. Theoretically the reaction may take place n either positions 2 or 5.

<sup>2</sup> Unpublished part of thesis, U. W.

of the solution, the residues varying in color from brown ( $1/10$  mol.) to almost black (1 mol. of thymoquinone). The color of the residues of the  $\text{NaHSO}_3$  experiments were much lighter, varying from a light yellow to a brown. However, before evaporation the acidity of the solutions was tested by titration with  $N/2$  KOH V.S. using phenolphthalein as indicator. The results are herewith tabulated:

NaHSO <sub>3</sub> .	Thymoquinone.	Cc. $N/2$ KOH used.	Difference.
10.4 Gm.	Blank	196.9	24.7 cc.
10.4 Gm.	1.6 Gm. 0.1 mole	172.2	23.5 cc.
10.4 Gm.	3.2 Gm. 0.2 mole	149.7	29.5 cc.
10.4 Gm.	4.8 Gm. 0.3 mole	120.2	38.0 cc.
10.4 Gm.	6.4 Gm. 0.4 mole	82.2	18.6 cc.
10.4 Gm.	8.0 Gm. 0.5 mole	63.6	12.3 cc.
10.4 Gm.	9.6 Gm. 0.6 mole	51.3	25.9 cc.
10.4 Gm.	11.2 Gm. 0.7 mole	25.4	3.7 cc.
10.4 Gm.	12.8 Gm. 0.8 mole	21.7	4.6 cc.
10.4 Gm.	14.4 Gm. 0.9 mole	17.1	2.7 cc.
10.4 Gm.	16.8 Gm. 1.0 mole	14.4	

It becomes apparent that with three exceptions the amount of alkali used diminishes with each increase in the thymoquinone added. Ignoring for the moment the three irregularities, one would expect that according to equation No. 1 the amount of KOH set free, *i. e.*, neutralizing the  $\text{NaHSO}_3$  to  $\text{Na}_2\text{SO}_3$ , would be the same. However, this does not appear to be the case.

## THE ULTRAVIOLET TRANSMISSION OF LIQUIDS.\*

BY ELLERY H. HARVEY.

### INTRODUCTION.

This paper covers the development of a method for the measurement of the ultraviolet transmission (or absorption) of liquids, and records the results obtained on forty typical essential oils, seventeen fatty oils, sixteen representative crude oils and thirty miscellaneous liquids of cognate interest:

Briefly, the technic consists in determining the photochemical decomposition of an oxalic acid solution catalyzed with uranium acetate, by the ultraviolet radiation of a carbon arc, during two hours' exposure through a 3-mm. layer of water, and considering the amount of decomposition as 100%. The identical process is repeated, interposing each time between the source of light and the oxalic acid-uranium acetate solution a 3-mm. layer of the liquid under examination to act as a screen to the passage of the active rays. The more absorbent the liquid toward ultraviolet the less will be the amount of oxalic acid decomposed, hence the number of milligrams of oxalic acid decomposed in each instance when a screening liquid is used, referred to the amount decomposed when a transparent liquid like water is used as 100%, is a direct measure of the transmission (or conversely of the absorption) of the liquid under scrutiny.

### HISTORICAL.

The photochemical decomposition of aliphatic acids, particularly when catalyzed, has been known for many years. A brief history of the reaction with

\* Scientific Section, A. Ph. A., Rapid City meeting, 1929.