

Non-Volatile Acids

The still-residue, left after distilling off 19 liters from the cherry juice, was used for the investigation of the non-volatile acids by the ester distillation method.³ One-fifth of the distillation residue, equal to 19 liters of juice, was used.

The acids, separated from their lead salts, were converted into ethyl esters. The crude weight of the esters was 147 g. The ethyl esters were fractionated through an eight-inch (20-cm.) Widmer column with an electrically heated jacket at 10 mm. The boiling points and yields of the three fractions were as follows:

Fraction 1	84-86°	6.3 g.
Fraction 2	125-128°	125.0 g.
Fraction 3	about 160°	very little

To seven-tenths of a gram of each fraction in 5 cc. of absolute alcohol, 2 cc. of hydrazine hydrate solution was added.

Fraction 1 gave no crystalline hydrazide. Neither oxalic acid nor succinic acid was found. When the fraction was saponified, a crystalline acid was obtained which did not melt. Optical crystallographic examination⁴ showed that this acid is fumaric acid. It is probably formed by the dehydration of malic acid and is not present in the juice.

Fraction 2 gave a copious precipitate, which was shown

(3) Franzen and Helwert, *Z. physiol. Chem.*, **122**, 46-85 (1922); Nelson, *THIS JOURNAL*, **46**, 2337 (1924), and **47**, 568 (1925).

(4) Optical crystallographic examinations were made by G. L. Keenan of the Food and Drug Administration.

by melting point (178.5°) and mixed melting point to be malic hydrazide.

Fraction 3 gave a hydrazide, which, after recrystallization, was shown by optical crystallographic examination to be identical with the hydrated form of citric trihydrazide. The quantity was insufficient for a melting point determination.

Franzen and Helwert³ found a trace of oxalic acid, small amounts of succinic and citric acids, and malic acid predominating, in cherries examined by them. However, neither oxalic nor succinic acid was found in Montmorency cherries by the present writers.

Summary

The flavor of pitted Montmorency cherry juice was found to be due mainly, if not entirely, to benzaldehyde (2.8 mg. per liter in the sample examined) and possibly in part to a trace of an alcohol having a rose-like odor, probably geraniol.

From ninety-four liters of juice there was obtained about 10 cc. of mixed alcohols, boiling at 73-76°, which consisted of 35% methyl and 65% ethyl alcohol.

The non-volatile acids of Montmorency cherries were found to consist chiefly of malic acid, and a very small amount of citric acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Cleavage of Benzyltrimethylphenylammonium Chloride by Certain Sulfur-containing Salts (I)

BY H. R. SNYDER AND J. C. SPECK

Considerations of the structural similarity between the pyrimidine and benzene rings made it seem likely that the cleavage of thiamin (vitamin B₁) by sodium bisulfite¹ (equation A) is a manifestation of the well-known lability of the bond between the benzyl group and the nitrogen atom of benzylamine derivatives. Von Braun² found that the benzyl group is among the radicals most readily removed in the cleavage of tertiary amines with cyanogen bromide. Embde and Kull³ and more recently Achmatowicz and Lindenfeld⁴ have shown that the benzyl radical is removed readily from quaternary ammonium salts by hydrogenation. Tschugaeff and Chlopin⁵ reported that

(1) Williams, Waterman, Keresztesy and Buchman, *THIS JOURNAL*, **57**, 536 (1935).

(2) Von Braun and Weiszbach, *Ber.*, **63**, 490 (1930).

(3) Embde and Kull, *Arch. Pharm.*, **274**, 173 (1936).

(4) Achmatowicz and Lindenfeld, *Roczniki Chem.*, **18**, 75 (1938); *C. A.*, **32**, 9047 (1938).

(5) Tschugaeff and Chlopin, *Ber.*, **47**, 1272 (1914).

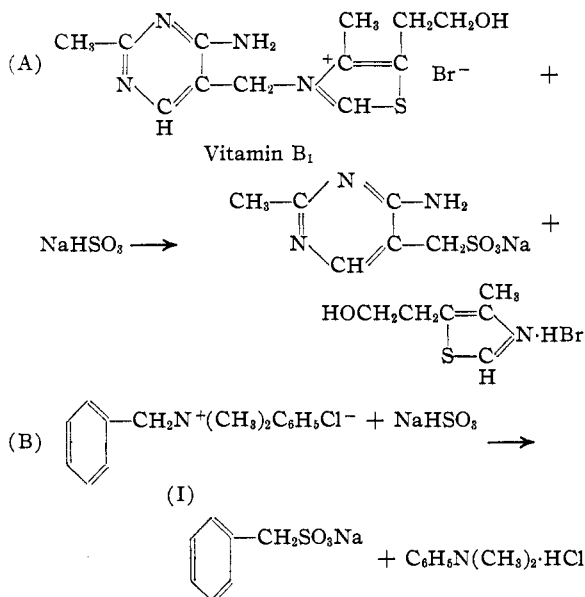
benzyltrimethylphenylammonium chloride in aqueous solution converts sodium telluride to benzyl telluride. Baw⁶ observed that the same ammonium salt may be used to benzylate phenols in alkaline solutions. In addition Porai-Koschitz⁷ has studied the benzylating action of this quaternary salt, but the details of his work apparently are not available in this country.

In view of these observations it was desirable to determine whether quaternary ammonium salts containing the benzyl group will undergo scission on mild treatment with sodium bisulfite (equation B).

A study of benzyltrimethylphenylammonium chloride (I) has revealed that it is cleaved in the expected manner not only by aqueous sodium bisulfite, but also by solutions of sodium sulfite, so-

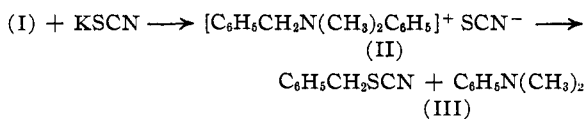
(6) Baw, *Quart. J. Indian Chem. Soc.*, **3**, 101 (1926).

(7) Porai-Koschitz, *C. A.*, **29**, 7957 (1935).

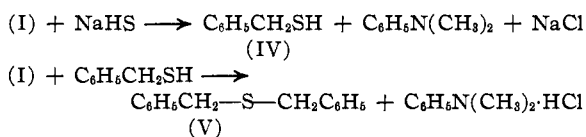


dium hydrosulfide, sodium sulfide, sodium thiosulfate and potassium thiocyanate. Cleavage is effected by these reagents when the solutions are kept at the boiling point for one hour. Under the same conditions sodium cyanide, sodium phenoxide, sodium borate, sodium hydroxide and tri-sodium phosphite are ineffective.

The behavior of the quaternary salt toward potassium thiocyanate yields information concerning the mechanism of these cleavage reactions. When cold solutions of the reactants are mixed benzyl dimethylphenylammonium thiocyanate (II) precipitates immediately. Under the influence of heat this rearranges to benzyl thiocyanate (III) and dimethylaniline.

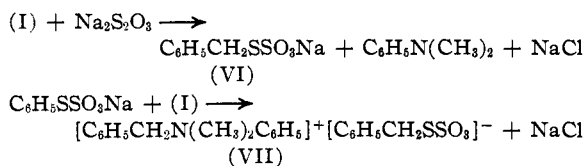


When sodium hydrosulfide is used the major product is benzyl sulfide (V) rather than the expected mercaptan (IV). The mercaptan must therefore be alkylated more rapidly by the quaternary salt than is the hydrosulfide ion. Sodium sulfide also gives good yields of benzyl sulfide.



Sodium thiosulfate cleaves the quaternary salt rapidly to give dimethylaniline and sodium S-benzyl thiosulfate (VI). The latter reacts with a

second molecule of the ammonium salt to form the relatively insoluble benzyl dimethylphenylammonium S-benzyl thiosulfate (VII). This salt may also be prepared directly from sodium S-benzyl thiosulfate obtained by the method of Purgotti,⁸ and the quaternary salt.



Sodium bisulfite gives dimethylaniline and sodium α -toluenesulfonate. The yields are considerably lower than those given by sodium sulfite. It was observed that during reaction with bisulfite a copious evolution of sulfur dioxide occurs. A part of the bisulfite is therefore destroyed by the acid liberated in the reaction. Since sodium sulfite, which gives good yields, must be converted to the bisulfite by the liberated acid, it is apparent that better results should be obtained with bisulfite if provision were made to replace the portion lost as sulfur dioxide. It was found that the extent of cleavage is increased by the use of excess bisulfite. It should be noted that sulfite and bisulfite act on the ammonium salt much less rapidly than do thiosulfate, thiocyanate, sulfide and hydrosulfide.

Experiments to determine the effect of these reagents on quaternary salts containing other alkyl and aryl groups are in progress and will be reported later.

Experimental

The procedure employed, except as otherwise indicated, consisted in dissolving 24.8 g. (0.10 mole) of benzyl dimethylphenylammonium chloride in a solution of 0.10 mole of the reagent in 100 cc. of water. The resulting solution was heated to reflux for one hour. After cooling the reaction products were separated as described below.

Cleavage with Sodium Hydrosulfide.⁹—The reaction mixture was made strongly alkaline and extracted with ether. The ether solution was extracted with 5% hydrochloric acid. Dimethylaniline was obtained from the acid extract by treatment with alkali, extraction with ether, removal of the ether and distillation; yield 9.9 g. (82%); b. p. 187–192°. Benzyl sulfide was obtained from the acid-extracted ether solution above by evaporation and recrystallization from ether; yield 6.7 g. (54%); m. p. 49–50°. Benzyl thiol was obtained from the original alkaline solution by acidification, extraction with ether and distillation; yield 2.2 g. (18%); b. p. 190–195°.

(8) Purgotti, *Gazz. chim. ital.*, **20**, 25 (1890).

(9) Sodium hydrosulfide was prepared by bubbling hydrogen sulfide into a solution of sodium sulfide until the calculated increase in weight was obtained.

Cleavage with Sodium Sulfide.—The reaction mixture from 0.1 mole of the quaternary salt and 0.05 mole of sodium sulfide was acidified with concentrated hydrochloric acid and extracted with ether. Benzyl sulfide was obtained by evaporation of the ether; yield 8 g. (75%); a portion recrystallized from ether melted at 49–50°. Dimethylaniline was isolated from the acidified reaction mixture as described above; yield 8.2 g. (68%); b. p. 190–193°.

Cleavage with Potassium Thiocyanate.—Benzyl dimethylphenylammonium thiocyanate (II) precipitated immediately in nearly quantitative yields when the reaction mixture was prepared as described above. After crystallization from a mixture of alcohol and ether it melted at 104°.

Anal. Calcd. for $C_{16}H_{18}N_2S$: N, 10.37. Found: N, 10.26.

The reaction mixture after refluxing for one hour was acidified with hydrochloric acid and extracted with ether. Removal of the ether gave benzyl thiocyanate; yield 9 g. (60%). A portion recrystallized from ethyl alcohol melted at 43°. Dimethylaniline was obtained from the acid solution as described above; yield 8.2 g. (68%).

Cleavage with Sodium Bisulfite.—Sulfur dioxide was evolved when this reaction mixture was boiled. After cooling and addition of sodium hydroxide sodium- α -toluenesulfonate crystallized. This was identified by conversion to α -toluenesulfonyl chloride, m. p. 93°. Dimethylaniline was separated from the alkaline solution and from the sodium α -toluenesulfonate by extraction with ether and distillation; yield 2.9 g. (24%).

When the reaction was run with 0.20 mole of sodium bisulfite the yield of sodium α -toluenesulfonate was 12.3 g. (63%); the yield of dimethylaniline was 4.9 g. (40%).

Cleavage with Sodium Sulfite.—From the reaction¹⁰ of 0.03 mole of the quaternary salt and 0.04 mole of sodium

sulfite, heated in 50 cc. of water at 80° for five hours there was obtained 63% of dimethylaniline. The excess sulfite was removed from the aqueous solution with barium hydroxide. After removal of excess barium with carbon dioxide and evaporation of the solution to the point of crystallization there was obtained 82% of sodium α -toluenesulfonate.

When the reaction was carried out as described in the general procedure above there was obtained 7 g. (58%) of dimethylaniline.

Cleavage with Sodium Thiosulfate.—A solution containing 0.05 mole of sodium thiosulfate and 0.10 mole of the ammonium salt was boiled under reflux for one hour. After cooling the mixture was extracted with ether. A heavy ether-insoluble oil originally present crystallized during the extraction. From the ether there was obtained 6.0 g. (99%) of dimethylaniline. The crystalline material was found to be benzyl dimethylphenylammonium S-benzyl thiosulfate; yield 19.5 g. (94%); m. p., after crystallization from alcohol and ether, 104°.

Anal. Calcd. for $C_{22}H_{26}O_2NS_2$: C, 63.7; H, 6.03; N, 3.38; S, 15.42. Found: C, 63.61; H, 6.10; N, 3.31; S, 15.42.

A sample prepared from sodium S-benzyl thiosulfate⁸ and the quaternary salt melted at 104° and gave no depression in melting point when mixed with the above product.

Summary

Benzyl dimethylphenylammonium chloride is readily cleaved by aqueous solutions of sodium hydrosulfide, sodium sulfide, sodium thiosulfate, potassium thiocyanate, sodium bisulfite and sodium sulfite. In each case dimethylaniline is liberated and the benzyl group becomes attached to the sulfur atom of the reagent.

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An Investigation into the Causes of Gel Formation by Some Organic Salts in Methanol Solution

BY HERBERT HENSTOCK

The salting out of substances from aqueous solutions by means of both like and unlike ions is usually used as a method of precipitating them in more or less crystalline condition; comparatively few are thrown out in a gelatinous state. The use of organic substances as precipitants is necessarily confined to those which readily mix with water; the most frequent being alcohol, by the employment of which the first of a series of aqueous gels was produced with calcium acetate as the only solid,¹ and similar ones with sodium benzoate,²

and with potassium ethyl sulfate.³ In these communications it was also shown that, although these salts are only slightly soluble in ethanol, they exhibit marked solubility in methanol,⁴ from which they can be thrown out of solution as perfectly clear gels by organic liquids, many of these being immiscible with water. Since this work was published it has been found that a number of other salts of organic acids (see List I) readily form transparent gels in methanol solution with various organic liquids as dispersion media or pre-

(1) Henstock, *Trans. Faraday Soc.*, **29**, 1101 (1933).

(2) Henstock, *ibid.*, **30**, 560 (1934).

(3) Henstock, *ibid.*, **31**, 1 (1935).

(4) Henstock, *J. Chem. Soc.*, 1341 (1934).