COMMUNICATIONS TO THE EDITOR

LACTONE FORMATION IN THE SULFONATION OF HEAT TREATED ROSIN

Sir:

Some time ago Ruzicka and Meyer [*Helv. Chim. Acta*, **5**, 333 (1922)] described the formation of a lactone obtained on treating dihydroabietic acid with strong mineral acids. Apparently we have been able to obtain a similar, if not identical, lactone by sulfonation of heat treated rosin or heat treated abietic acid.

Fifty grams by weight of partially refined pseudopimaric acid [Brennan, Cairncross, Hasselstrom and Hull, U. S. Patent 2,072,628] melting point 167–169° (corr.), $(\alpha)^{31}D$ + 46.3°, and 250 g. of sulfuric acid, sp. gr. 1.84, were mixed at −5 to + 5°, and stirred for about twenty minutes. The brownish precipitate was collected, washed with cold water until the washing clouded when mixed with the original liquor, and the washed precipitate then extracted three times with boiling water, leaving a brownish insoluble, semi-solid rosin. The aqueous extracts on cooling deposited crystalline sulfonic acid in a yield of 25.5 g. After repeated crystallization from glacial acetic acid, it melted with decomposition at about 222–223° (uncorr.).

The brownish insoluble semi-solid rosin amounted to 30 g. When an acetone solution of this by-product was allowed to stand, it deposited 4 g. of a saturated lactone, a crystalline, white solid which, after recrystallization, melted at 130–131° (corr.). Calcd. for $C_{20}H_{32}O_2$: C, 78.9; H, 10.5. Found: C, 79.36, H, 10.51; C, 78.9, H, 10.79; C, 79.52, H, 10.73; C, 79.08, H, 10.53. The melting point of Ruzicka and Meyer's lactone was 130–131°.

The above lactone was saponified with 10% alcoholic potassium hydroxide solution for thirty-six hours. After evaporating the alcohol, the potassium salt of the hydroxy acid was dissolved in a large quantity of water and the hydroxy acid liberated with dilute acetic acid. The precipitated acid was purified through crystallization first from methanol–acetone, then from methanol and finally from hexane. The acid, fine white needles, melted at 161–162° (uncorr.), 165° (corr.) (dec.). Calcd. for $C_{20}H_{34}O_3$: C, 74.5, H, 10.6. Found: C, 74.73; H, 10.77.

The hydroxytetrahydroabietic acid of L. Ruzicka, H. Waldmann, Paul J. Meier and H. Hösli [*Helv. Chim. Acta*, **16**, 139–181 (1933)], obtained by saponification of the corresponding lactone, melted at 162–163°. Ruzicka and co-workers mention that the hydroxy acid is easily transformed into the lactone, which observation fully agrees with the properties of the hydroxytetrahydroabietic acid obtained by us. We have observed that the hydroxytetrahydroabietic acid when treated with acetyl chloride in the usual manner, yielded the lactone quantitatively which now melted at 131–131.5 (corr.); it did not lower the melting point when mixed with the lactone isolated from the original sulfonation product.

This investigation is being continued. Further information will be published at a later date.

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Received April 8, 1938

VITAMIN B-6

Sir:

We have reported the isolation of vitamin B-6 as its hydrochloride, m.p. 204–206° (dec.) elsewhere [*Proc. Exp. Biol. & Med.*, **38**, 64–65] (1938). Elementary analysis of the substance gives the empirical formula $C_8H_{12}NO_3Cl$. Calcd. for $C_8H_{12}NO_3Cl$: C, 46.70; H, 5.88; N, 6.81; Cl, 17.25. Found: C, 46.89, 46.79; H, 6.12, 6.10; N, 6.81, 6.94; Cl, 17.03, 17.13. Determinations of O—CH_3, N—CH_3 and water of crystallization were negative. It is optically inactive. The base itself, m.p. 160°, was isolated from the hydrochloride. *Anal.* Calcd. for $C_8H_{11}NO_3$: C, 56.80; H, 6.56. Found: C, 56.54, 56.84; H, 6.35, 6.15. Both the base and the hydrochloride readily sublime and final purification of the vitamin can be effected in this way. With ferric chloride the vitamin gives a reddish-brown coloration. The pure substance is stable to concentrated hydrochloric acid at elevated temperatures. It is not affected by heating with alkalies, nitrous acid, ethyl nitrate or Fehling's solution.

Since electrometric titration studies of the

hydrochloride show that there is but one break in the titration curve when all the chloride ion has been neutralized, the formula for the vitamin is $C_8H_{11}NO_3 \cdot HCl$.

The absorption spectrum studies of the vitamin hydrochloride in acid, alkaline and neutral solutions indicate that we are dealing with a compound with tautomeric properties.

Vitamin B-6 shows pronounced and well-defined absorption in the spectral region from 2300 to 3300 Å. In dilute hydrochloric acid (*p*H 2) there is a single band with maximum absorption at 2925 Å. The hydrochloride dissolved in water (*p*H 4.5) shows that the band at 2925 Å. diminished in intensity along with a new band with maximum absorption at 3275 Å. At *p*H 6.75 the band at 3275 Å. has increased markedly while that at 2925 Å. has disappeared and simultaneously a new band at 2560 Å. has appeared. At *p*H 10.2 the two bands which were present at *p*H 6.75 have increased in intensity and shifted toward the shorter wave lengths.

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RECEIVED APRIL 22, 1938

HYDROLYSIS OF SUCROSE

Sir:

In the literature on the hydrolysis of sucrose by acids no mention seems to have been made of the following effect, which we have observed experimentally.

The rate of inversion of 2% sucrose solutions by hydrochloric acid at various concentrations has been measured carefully at temperatures from 0 to 35°, using the dilatometric method. It has been observed that the energy of activation varies both with temperature, as already has been shown, and with the concentration of hydrochloric acid, which has not, we believe, been noted previously.

Choosing, for example, the temperature range from 0 to 10°, we find that the energy of activation varies from 24.2 kcal. at 4.842 molar hydrochloric acid to 26.2 kcal. at 1.1235 molar hydrochloric acid.

A possible explanation based on the theory of the transition state has been suggested for the concentration effect [private communication from Harold F. Walton, Princeton University].

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RECEIVED MARCH 25, 1938

AROMATIC AMINES AS CATALYSTS FOR THE DEHYDROGENATION OF GLYCERALDEHYDE

Sir:

Transformation of glyceraldehyde into pyruvic aldehyde (methyl glyoxal) by the catalytic action of aromatic amines in dilute acetic acid solution [Strain and Spoehr, *J. Biol. Chem.*, **89**, 527 (1930)] may be regarded as an intramolecular hydrogenation–dehydrogenation reaction. In the presence of amines and hydrogen acceptors (oxygen, methylene blue and indigo carmine) hydrogen is removed from the glyceraldehyde. This dehydrogenation yields a mixture of carbonyl compounds as is shown by the formation of phenylhydrazine and 3-nitrobenzohydrazine derivatives and their chromatographic adsorption. Reaction of glyceraldehyde with oxygen in the presence of amines is accompanied by the formation of peroxides and colored insoluble products. Pyruvic aldehyde itself does not reduce methylene blue in the presence of amines, and dihydroxyacetone exhibits only a slow reducing action. Substances which might be expected to occur as dehydrogenation products of glyceraldehyde such as those produced by oxidation of dihydroxyacetone with cupric acetate [Evans and Waring, THIS JOURNAL, **48**, 2678 (1926)] exhibit very strong reduction. Intermolecular oxidation and reduction of glyceraldehyde and its intermediate transformation products may account for the variations in the yields of pyruvic aldehyde previously observed (Ref. 1, p. 532). These observations also indicate that aromatic amines may be regarded as catalysts (analogous to dehydrogenases) for the dehydrogenation of glyceraldehyde as well as for the molecular rearrangement of glyceraldehyde to pyruvic aldehyde.

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