Summary.

The pyrosulfates of sodium and potassium are convenient and effective as mild condensing agents.

Good results were obtained by means of these agents in the preparation of triphenylbenzene, benzal-aniline, benzalmalonic acid, benzal-acetophenone, and acetanilide.

The pyrosulfates cannot be used to condense the phenols with other substances.

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A CHEMICAL INVESTIGATION OF THE OIL OF CHENOPODIUM. II.

BY E. K. NELSON.

Rearrangement of Ascaridole.—As shown by Schimmel's chemists[1] ascaridole suffers a molecular rearrangement when heated with caution to 150°, while the author has found[2] that hydration of ascaridole by shaking it with solution of ferrous sulfate affords the same glycol which is obtained by hydrating the conversion product obtained by heating. This shows that the formation of glycol on treatment with ferrous sulfate must be accompanied by the same rearrangement which takes place on heating ascaridole.

The rearrangement of ascaridole by heating it to 150° and the substances obtained by shaking the conversion product with dilute sulfuric acid have been further studied. It has been found that in addition to the glycol which has been already described, and which is the chief product, two other crystallin water soluble substances are formed, one in considerable, the other in lesser amount. As these products are quite easily decomposed by the action of mineral acids, it was found necessary, in order to obtain them, to use very dilute sulfuric acid in hydrating. The conversion product was prepared[3] and rectified by distillation at 4 mm. Fifty grams of the product were stirred for 2 hours with 500 cc. of 0.2% sulfuric acid, the oil going almost completely into solution. The glycol of m. p. 62.5–64° was extracted directly from the solution with ether, the residue from which crystallized on seeding with the solid substance.

The acid solution was exactly neutralized, concentrated to about one-fifth its volume, and extracted with chloroform. A sirupy residue was obtained from the chloroform, which, after adding a very little water, became crystallin on standing. The substance thus isolated in small

[1] *Schimmel's Report*, April, 1908.

[2] THIS JOURNAL, **33**, 1404.

[3] *Schimmel's Report*, April, 1908; THIS JOURNAL, **33**, 1404.

amount is easily soluble in water, difficultly soluble in benzene. It crystallizes with one molecule of water, which is lost on gentle drying.

The anhydrous substance melts at 103–105°.

Analysis of the Hydrated Substance.

<div style="margin-left:2em">
Calculated for $C_{10}H_{18}O_3 + H_2O$: C, 58.77;   H, 9.87.

Found: C, 58.52, 58.72; H, 9.88, 9.92.
</div>

Analysis of the Anhydrous Substance.

<div style="margin-left:2em">
Calculated for $C_{10}H_{18}O_3$: C, 64.46; H, 9.74.

Found: C, 64.25; H, 9.85.
</div>

This glycol, designated as the β-glycol to distinguish it from the one previously found, is decomposed on warming with dilute sulfuric acid, thymol being formed. The thymol was identified by its melting point, 50–51°, and the melting point of its phenylurethane, 103–104°. The phenylurethane was completely soluble in petroleum ether, thus proving the absence of carvacrol.

The solution from the chloroform extraction was evaporated to a sirupy consistency and further dried as thoroughly as possible in a vacuum desiccator in a shallow dish. After some time it became crystallin. Sirupy impurities were removed by washing with ether, in which the substance is scarcely soluble, and 7 grams of the product obtained. This was freed from inorganic salts by solution in absolute alcohol and further purified by crystallizing from boiling chloroform.

The substance, dried in a vacuum oven, melts at 128–130°. It is *very easily* soluble in water or alcohol, difficultly soluble in ether or chloroform.

Analysis of the desiccated material gave

<div style="margin-left:2em">
Calculated for $C_{10}H_{20}O_4$: C, 58.77; H, 9.87.

Found: C, 58.66; H, 9.93.
</div>

Analysis of the undried substance gave figures agreeing with those calculated for one molecule of water of crystallization.

<div style="margin-left:2em">
Calculated for $C_{10}H_{20}O_4 + H_2O$: C, 54.01;   H, 9.98.

Found: C, 54.46, 54.41; H, 10.06, 10.02.
</div>

When this "erythrite" is boiled with dilute sulfuric acid it is decomposed. The products of dehydration have not as yet been thoroughly studied, but a ketone with strong menthone odor and a peculiar crystallin phenolic substance, melting at 80–81°, have been separated. The semicarbazone of the ketone melted at 182–184° and was difficultly soluble in the ordinary solvents. This melting point is much lower than that reported by Wallach for the semicarbazone of Δ^1-menthenone, melting at 224–226°, and obtained as a product of dehydration from 1,3,4-trihydroxyterpane, so that possibly we have here an isomeric menthenone, or a mixture of isomers.

On the basis of the formula proposed by the author for the glycol anhydride, which is the product formed on heating ascaridole to 150°,

it is not easy to account for the formation of the erythrite. The glycol anhydride distilled over within $1°$ (98.5–$99.5°$ at 4 mm.), but repeated fractionation failed to effect a separation, as the first and last fractions gave the same hydration products in the same proportion. Neither could the erythrite be obtained from the α-glycol on further shaking with dilute sulfuric acid.

Since the author's first contribution on this subject, and while the present work was in progress, Wallach[1] has published the results of his work on ascaridole. Wallach assigns a different structure to ascaridole from that proposed by the author in that he finds it to be a 1,4 (I) instead of a 3,6-peroxide.

I.   II.   III.
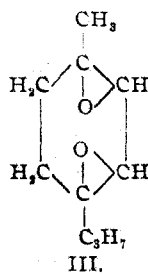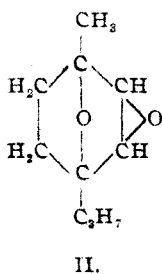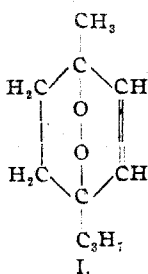
On the basis of this formula, which is well supported by facts, it is easier to account for the fact that the hydration of the rearrangement product leads to the formation of more than one glycol.

Starting with ascaridole two rearrangements suggest themselves to produce the glycol anhydrides.

The structure represented by III probably is that of the conversion product obtained on heating ascaridole to $150°$. It is the simplest one, and on hydration it should form 1,2,3,4-tetrahydroxymenthane (1,2,3,4-tetrahydroxyterpane) (IV). At the same time it is quite an unstable dioxide and may go through the more stable form II to form the glycol V.

IV.   V.
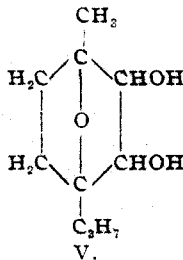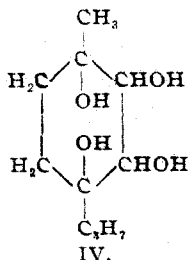
If the erythrite possesses the structure IV it should be easily oxidized to αα'-dihydroxy- α, α-methylisopropyladipic acid.

Oxidation of the Erythrite.—The erythrite, 11 grams, was dissolved in

[1] *Ann.*, 392, 59.

300 cc. water, and the solution added to an ice cold solution of 15 grams of potassium permanganate and 10 grams of potassium hydroxide in 500 cc. water, the mixture being stirred until the permanganate color had disappeared. The filtered solution was saturated with carbon dioxide, evaporated to dryness, and the organic salts extracted with alcohol. The residue from the alcohol was dissolved in water, the acids liberated with dilute sulfuric acid, the solution shaken out once with ether, and finally exhausted with acetic ester. The latter solvent removed an acid which was difficultly soluble in ether and only moderately soluble in hot water or acetic ester. Recrystallized twice from a large volume of hot water it appeared as well formed, rhombic prisms melting at 190–191°, losing water when heated above the melting point.

The acid gave on analysis,

Calculated for $C_{10}H_{18}O_6$: C, 51.25;   H, 7.76.
Found: C, 50.84, 50.87, 51.09; H, 8.07, 8.06, 8.15.

When the acid was heated above its melting point very unexpected results were observed. When thus treated it behaves quite differently from the similar acids described by Wallach[1] as no dilactone is obtained, either on heating alone or with concentrated hydrochloric acid. When heated to 210° it passes into its anhydride, a water soluble substance from which the acid is regenerated on boiling with water.

On heating further to 250° for a short time the odor of methyl heptenone could be noticed, and an anhydride is formed which is not soluble in water, but which on boiling with water forms an acid crystallizing in needles and which melts at 116–117°, showing no depression in melting point when mixed with "ascaridic" acid, $C_{10}H_{16}O_5$, which was obtained as the chief oxidation product of the α-glycol.[2]

The melting point of the insoluble anhydride, crystallized from benzene, is 70–71°, which is also the melting point of the anhydride of "ascaridic" acid.

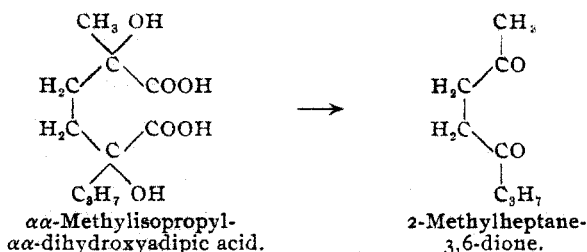Of the four possible active modifications of $\alpha\alpha$-methylisopropyl-α,α-dihydroxyadipic acid, while two would be likely to form dilactones, the other two would tend to form the acid anhydrides, losing water further between the hydroxyl groups.

Oxidation of the Acid, $C_{10}H_{18}O_6$.—As Wallach has shown,[3] a diketone, 2-methylheptane-3,6-dione (ω-dimethylacetonylacetone), is formed on oxidizing $\alpha\alpha$-methylisopropyl-α,α-dihydroxyadipic acid by means of potassium permanganate in acid solution.

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[1] *Ann.*, **356**, 211.

[2] THIS JOURNAL, **33**, 1404.

[3] *Ann.*, **362**, 263.

CH₃ OH ... structures

$$\begin{array}{cc}
\text{CH}_3\ \text{OH} & \text{CH}_2 \\
\backslash/ & | \\
\text{C} & \text{CO} \\
\text{H}_2\text{C}\diagup\ \diagdown\text{COOH} & \text{H}_2\text{C}\diagup \\
| & | \\
\text{H}_2\text{C}\diagdown\ \diagup\text{COOH} & \text{H}_2\text{C}\diagdown \\
\text{C} & \text{CO} \\
\diagup\diagdown & | \\
\text{C}_3\text{H}_7\ \text{OH} & \text{C}_3\text{H}_7
\end{array}$$

$\rightarrow$

αα-Methylisopropyl-   2-Methylheptane-
αα-dihydroxyadipic acid.   3,6-dione.

The acid (less than a half gram being available), was oxidized with potassium permanganate in the presence of sulfuric acid according to the directions given by Wallach, and the product distilled with steam. An oil with a peculiar odor was extracted from the distillate which reacted readily with semicarbazine. The semicarbazone, crystallized from alcohol, melted at 201–202° and gave a distinct pyrrole reaction when heated in a test tube in which was placed a pine splinter moistened with hydrochloric acid, which agrees with the data recorded for the semicarbazone of 2-methylheptane-3,6-dione. This ketone, as will be shown, was further more fully identified as a product of the oxidation of the acid $C_{10}H_{16}O_5$ which was obtained by the oxidation of the α-glycol and also as a dehydration product of the acid $C_{10}H_{18}O_6$.

There seems no doubt, therefore, that the acid $C_{10}H_{18}O_6$ is one of the modifications of αα-methylisopropyl-αα-dihydroxyadipic acid, differing in its properties from the two previously described by Wallach.

Oxidation of the Acid $C_{10}H_{16}O_5$.—The acid $C_{10}H_{16}O_5$, which was obtained on oxidation of the α-glycol as well as a dehydration product of "iso"-αα-methylisopropyl-αα-dihydroxyadipic acid, was further oxidized by means of acid potassium permanganate to 2-methylheptane-3,6-dione. The semicarbazone melted at 201–202° and gave the pyrrole reaction. When mixed with the semicarbazone of 2-methylheptane-3,6-dione, prepared by oxidation of β-thujaketocarbonic acid, no depression of melting point was observed. The dioxime was prepared by allowing the ketone, in alcoholic solution, to stand for an hour with an excess of hydroxylamine hydrochloride and a little less than the amount of sodium bicarbonate necessary to set free the base. Thus prepared the dioxime was difficultly soluble in acetone. Recrystallized in fine needles from hot acetone it melted at 130–131°. Semmler[1] and Harries[2] have found the dioxime to melt at 132°, while Wallach[3] reports a melting point of 137°.

Energetic oxidation of the α-glycol also afforded a good yield of 2-methylheptane-3,6-dione, identified by its semicarbazone and dioxime.
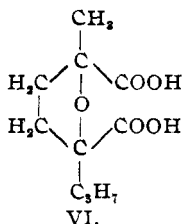
Conclusions as to Structure.—In the light of the foregoing data the

[1] *Ber.*, **30**, 433.
[2] *Ibid.*, **35**, 1182.
[3] *Ann.*, **362**, 264.

structure of the α-glycol must be as represented (V), of the erythrite as (IV), and the acid obtained on oxidation of the α-glycol must possess the structure of 1,4–cineolic acid (VI).

$$
\begin{array}{c}
CH_3 \\
| \\
C \\
H_2C \diagup \; | \; \diagdown COOH \\
| \quad O \\
H_2C \diagdown \; | \; \diagup COOH \\
C \\
| \\
C_3H_7
\end{array}
$$

VI.

As has been mentioned[1] the odor of methyl heptenone was apparent when the 1,4-cineolic acid was heated considerably above its melting point. Several attempts have since been made to identify methylheptenone without success. The conversion of 1,4-cineolic acid into methylheptenone requires the transference of one hydrogen atom to the adjacent position, the reaction not being so simple as in the case of the ordinary cineolic acid. Therefore, while probably a trace of methylheptenone was formed from the 1,4-cineolic acid, the yield would not be expected to be very large.

Action of Saturated Oxalic Acid Solution on the Glycol Anhydride.— Twenty-five grams of the glycol anhydride were boiled for 4 hours with 150 cc. of a saturated solution of oxalic acid. The oil which separated was extracted with a 5% solution of potassium hydroxide and the alkalin liquid distilled with steam. A crystallin substance was obtained in small amount from the distillate, which possesses weak phenolic properties. Recrystallized from dilute alcohol it appeared as fine needles with a faint phenolic odor, melting at 80–81°. The crystals were slightly soluble in water. The aqueous, as well as the hydro-alcoholic solution, afforded a deep blue color with ferric chloride.

Analysis gave

        Calculated for $C_{10}H_{16}O_2$: C, 71.37;   H, 9.59.
        Found: C, 71.56, 71.13; H, 9.74, 9.66.

The same substance was also obtained in small amount on treating the α-glycol with strong dehydrating agents, and, as was already noted, on boiling the erythrite with dilute sulfuric acid. It is isomeric with diosphenol, but differs from it in not reducing Fehling's solution or an ammoniacal solution of silver nitrate. Hydroxylamine and semicarbazine do not react with it under the ordinary conditions. When boiled with a strongly alkalin solution of hydroxylamine for several hours it is changed, but no definit crystallin oxime has so far been obtained. Under these severe conditions it is questionable whether the compound may not pass from the enol to the keto form. The presence of a car-

[1] This Journal, 33, 1404.

bonyl group seems therefore improbable. Considering the question of stability together with the fact that, as will be shown, carvacrol is obtained as a product of the dehydration of the glycol anhydride, it seems altogether probable that it results from the rearrangement of the anhydride in the following manner:

Glycol anhydride.   "Oxy" phenol.
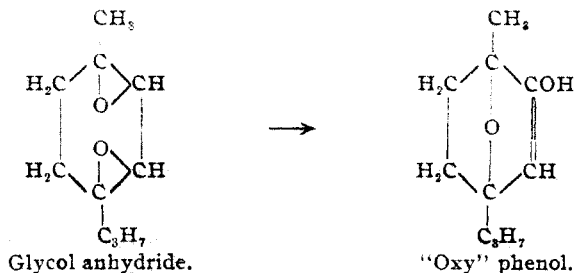
Dehydration of the Glycol Anhydride.—In an attempt to form an ester by the direct union of the glycol anhydride with benzoic anhydride, the mixture was heated to 150°. The expected result was not obtained, water being split off and a phenol ester obtained, from which the phenol was isolated and purified by solution in 5% potassium hydroxide. This phenol proved to be carvacrol. Analysis agreed with the formula $C_{10}H_{14}O$. Sp. gr. 20° 0.9756 n_D 20°, 1.522. Phenylurethane, m. 140°. The yield amounted to about 25%.

THE VOLATIL ALIPHATIC ACIDS OF CORN SILAGE.

BY ARTHUR W. DOX AND RAY E. NEIDIG.

In view of the recent publication in THIS JOURNAL of an article by Hart and Willaman[1] entitled "Volatil Fatty Acids and Alcohols in Corn Silage," it is thought advisable to call attention to a previous publication of our own[2] on the same subject. The present paper is not simply a claim to priority on the part of the authors, but an endeavor to explain the discrepancy between our results and those obtained by Hart and Willaman.

The method used by Hart and Willaman in preparing their sample for the Duclaux determination is briefly as follows: The silage was first ground in a food chopper. One hundred grams were suspended in two liters of water, 10 cc. of concentrated sulfuric acid were added and the solution was distilled in a current of steam until a distillate of three liters was collected. The distillate was neutralized with barium hydroxide

[1] THIS JOURNAL, 34, 1619–25 (1912).
[2] Dox and Neidig, "The Volatile Aliphatic Acids of Corn Silage," Iowa Agricultural Experiment Station, *Research Bulletin* 7, 32, June, 1912. This publication may be had free of charge upon application to the authors or to the Director of the Iowa Agricultural Experiment Station, Ames, Iowa.