filtered, the volume brought to 300 cc., 2 cc. of 3 *N* hydrochloric acid added and the precipitation of barium sulfate carried out in the usual manner.

Much time may be saved if the estimation of sulfate is performed volumetrically. In this case the filtered acid solution is brought to a volume of 200 cc. and handled as directed in a previous paper on this subject.[5]

Results

Table I cites results secured in the analysis of several organic compounds by this method. The first three compounds are solids. They were analyzed to insure that the method would handle compounds known to be difficult of oxidation or because they had been analyzed by other methods and their sulfur content was known.

Summary

The Klason method of oxidation of volatile organic liquids and solids as reported in modified form by Leonard has been altered so as to replace the expensive platinum catalyst with chips of pyrex glass. Air is used in place of oxygen, thus greatly decreasing the possibility of flashing. The method is recommended for the determination of sulfur in organic liquids and in solids for which the Parr method is unsuitable.

FAYETTEVILLE, ARKANSAS

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. II. THE DERIVATIVES OF DERRITOL[1]

BY F. B. LAFORGE AND L. E. SMITH

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Catalytic hydrogenation of rotenone results in the formation of two compounds: dihydrorotenone, a neutral substance in which the original double bond is reduced, and an acid product which still contains the double bond. Both compounds on further reduction yield an acid containing four more hydrogen atoms than rotenone. The acid of formula $C_{23}H_{24}O_6$ will be referred to as rotenonic acid and its reduction product as dihydrorotenonic acid.[2]

This peculiar course of the reduction of rotenone leading to an acid product is characteristic not only of rotenone, but of several of its derivatives.

The action of zinc in alkaline solution on rotenone also results in the formation of two compounds: rotenol, in which the carbonyl group is reduced to an alcoholic group, and a yellow phenolic compound, derritol,

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[5] Wertheim, THIS JOURNAL, **52**, 1075 (1930).

[1] Presented before the Division of Agricultural and Food Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minnesota, September 9 to 13, 1929.

[2] LaForge and Smith, THIS JOURNAL, **51**, 2574 (1929).

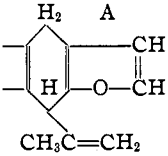
with composition $C_{21}H_{22}O_6$, two carbon atoms having been lost from the rotenone molecule.[3] Dihydrorotenone yields two analogous compounds.

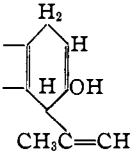
In order to decide whether or not the same groupings were involved in these two characteristic reactions of rotenone toward two different reducing agents, derritol itself was reduced with hydrogen in the presence of platinum catalyst. In all probability it yielded dihydroderritol and derritolic acid, but since the separation of these substances was very difficult, it was found preferable first to methylate the phenolic group in order to render the neutral compound resulting from the reduction insoluble in alkali. Methyl derritol is easily obtained by the action of dimethyl sulfate on derritol in alkaline solution.

The methylated compound gave on hydrogenation a mixture of dihydromethylderritol and methylderritolic acid. From the result of this reaction it follows that the atomic groupings in rotenone which on hydrogenation react to produce an acid are not the same as those groupings which react with zinc in alkaline solution to produce derritol.

According to Takei,[4] tubaic acid, and hence rotenone, contains the atomic grouping A. If this formulation is correct, derritol would be expected to result by the loss of two carbon atoms from this grouping, with the formation of a phenolic radical at one of the points of attachment, although it seems strange that the double bond in the furan ring would escape reduction on catalytic hydrogenation.

A





Derritol

Rotenol gives dihydrorotenol and dihydrorotenolic acid on catalytic hydrogenation.

Derritol Methyl Ether.—One gram of derritol was dissolved in the equivalent amount of 1% potassium hydroxide and 0.5 g. of dimethyl sulfate was slowly added to this solution with constant stirring. Derritol methyl ether separated out and was filtered off and recrystallized from methyl alcohol, m. p. 122°. The yield was quantitative.

Anal. Subs., 0.0609, 0.0640: CO_2, 0.1525, 0.1603. Subs., 0.0264, 0.0256; AgI, 0.0483, 0.0471. Calcd. for $C_{22}H_{24}O_6$: C, 68.75; H, 6.25; $3CH_3O$, 24.21. Found: C, 68.30, 68.32; H, 6.37, 6.32; CH_3O, 24.15, 24.31.

Reduction of Derritol Methyl Ether.—One gram of derritol methyl ether was reduced in ethyl acetate solution, 0.2 g. of platinum oxide catalyst[5] previously saturated with hydrogen being used. The theoretical volume of hydrogen corresponding to 1 molecule is 58.4 cc. The solution absorbed 60 cc. in a few minutes, after which the rate became very slow. The reaction was stopped at this point.

The solution was filtered and after the ethyl acetate had been boiled off the residue was taken up in ether and the ether solution extracted with 2% potassium hydroxide

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[3] Butenandt, *Ann.*, **464**, 274 (1928).

[4] S. Takei, *Abstracts from Bull. Inst. Physical and Chemical Research* (*Japan*), **8**, 64 (1929).

[5] R. Adams and R. L. Shriner, This Journal, **45**, 2171 (1923).

solution. The ether solution was washed with water, dried over anhydrous sodium sulfate and the solvent was evaporated. The compound, dihydroderritol methyl ether, was recrystallized from 95% ethyl alcohol, m. p. 107°, yield 0.17 g.

Anal. Subs., 0.0735: CO_2, 0.1838; H_2O, 0.0445. Subs., 0.0197; AgI, 0.0358. Calcd. for $C_{22}H_{26}O_6$: C, 68.39; H, 6.74; $3CH_3O$, 24.1. Found: C, 68.19; H, 6.73; CH_3O, 24.0.

The aqueous alkaline solution was acidified with hydrochloric acid, extracted with ether and the ether solution was dried over sodium sulfate. The compound methylderritolic acid was recrystallized from benzene; m. p. 154–156°; yield, 0.75 g.

Anal. Subs., 0.0775, 0.0521: CO_2, 0.1935, 0.1305; H_2O, 0.0483, 0.0329. Subs., 0.0203: AgI, 0.0379. Calcd. for $C_{22}H_{26}O_6$: C, 68.39; H, 6.74; $3CH_3O$, 24.1. Found: C, 68.07, 68.31; H, 6.92, 7.01; CH_3O, 24.66.

Oxime of Derritol Methyl Ether.—One-half gram of derritol methyl ether was refluxed for four hours with 0.4 g. of hydroxylamine hydrochloride and 0.5 g. of anhydrous sodium acetate in absolute ethyl alcohol. Upon dilution with water, the oxime crystallized out and was recrystallized from dilute ethyl alcohol, m. p. 172–173°.

Anal. Subs., 0.0565: CO_2, 0.1371; H_2O, 0.0333. Subs., 0.0203: AgI, 0.0355. Calcd. for $C_{22}H_{25}O_6N$: C, 66.16, H, 6.26; $2CH_3O$, 23.3. Found: C, 66.16; H, 6.55; CH_3O, 23.09.

Reduction of Rotenol.—One gram of rotenol was reduced with hydrogen in ethyl acetate solution; 0.2 g. of platinum oxide catalyst was used. The theoretical volume of hydrogen corresponding to 1 molecule is 56.6 cc. The solution absorbed about 75 cc. very rapidly, after which the rate of absorption began to decrease. It was found that if the reaction was stopped at this point the alkali-soluble product was a mixture of two acids. The reaction was, therefore, prolonged until 90 cc. of hydrogen had been absorbed. The ethyl acetate was evaporated off and the residue dissolved in ether and divided into neutral and acid parts. The neutral portion proved to be dihydrorotenol identical with that prepared from dihydrorotenone.[2] The yield was 0.15 g. The acid portion, dihydrorotenolic acid, was recrystallized from dilute ethyl alcohol. It melted between 76 and 80°, and probably contained an indefinite amount of solvent. The yield was 0.75 g. For analysis it was dried to constant weight at about 90°.

Anal. Subs., 0.0560, 0.0494: CO_2, 0.1415, 0.1249; H_2O, 0.0352, 0.0305. Subs., 0.0223: AgI, 0.0264. Calcd. for $C_{23}H_{28}O_6$: C, 69.0; H, 7.0; $2CH_3O$, 15.5. Found: C, 68.92, 68.95; H, 6.74, 6.86; CH_3O, 15.64.

Summary

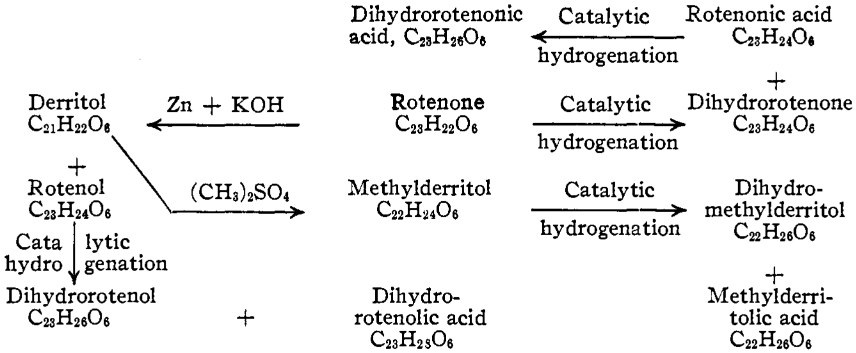
Both derritol and rotenol give mixtures of neutral and acid products on catalytic hydrogenation.

In the case of derritol, which is itself a phenolic compound, it was necessary to methylate the phenol group for convenience in separating the acid. Dihydromethylderritol and methylderritolic acids were the products of the reduction.

Rotenol gave dihydrorotenol and rotenolic acid. The latter was further reduced to dihydrorotenolic acid.

These results indicate that the atomic groupings which react to form derritol from rotenone are not the same as those which are involved in the formation of acids from rotenone and many of its derivatives.

The reactions involved are illustrated in the diagram shown below.



WASHINGTON, D. C.

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

ROTENONE. III. DEHYDROROTENONE[1]

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Butenandt[2] has shown that a number of oxidizing agents, such as permanganate, potassium ferricyanide, perbenzoic acid and iodine with potassium acetate in alcoholic solution, convert rotenone into dehydrorotenone with a loss of two hydrogen atoms.

Dehydrorotenone is a yellow crystalline compound melting at about 225° and differing widely from rotenone in most of its reactions. Compounds corresponding to dehydrorotenone are easily obtainable from dihydrorotenone and isorotenone. Dehydrorotenone contains the original double bond and carbonyl group of rotenone, but unlike rotenone, it is not decomposed by alkalies, nor does it yield a compound corresponding to derritol. On treatment with alkali or with zinc in alkaline solution, it takes up two molecules of water and is converted into an acid[2] $C_{23}H_{24}O_8$ which for future reference we would like to call dehydrodihydroxyrotenonic acid.

When rotenone is subjected to treatment with stronger oxidizing agents, such as chromic or nitrous acid, the resulting product is a bright yellow compound, rotenonone, having the composition either $C_{23}H_{20}O_7$ or $C_{23}H_{18}O_7$. It is sometimes difficult to prepare rotenonone in a pure state since hydrochloric acid is likely to be added to the double bond. However, dihydrorotenone readily yields dihydrorotenonone on treatment with nitrous acid and corresponding compounds are easily obtained from isorotenone, rotenonic and dihydrorotenonic acids.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 78th Meeting of the American Chemical Society, Minneapolis, Minn., September 9 to 13, 1929.

[2] Butenandt, *Ann.*, **464**, 270 (1928).