equivalent to 3.25 g. of the dibromide), 17 g. of resin, and 2.85 g. lost or unidentified. A weight of propylene that would be equivalent (2 moles) to the phenetidine formed would be 3.24 g. No monoallylphenetidine was found. Its stability at the reflux temperature of 275° is evidently less than that of allylaniline at 240°.

Pyrolysis. Two Hours of Reflux.—A 30-g. sample of diallyl-*p*-phenetidine on refluxing for two hours in an all-glass apparatus gave 10.6 g. of liquid products, 16.5 g. of resin and 2.65 g. of propylene. The phenetidine in the liquid products amounted to 8.07 g. These results are almost identical with those obtained with the forty-four hours reflux period. The greater recovery of propylene in this instance is due to the fact that the gas was collected as such and was not subjected to the unavoidable losses occasioned by its conversion into propylene dibromide.

## Summary

The behavior of allylaniline, diallylaniline and diallyl-*p*-phenetidine at elevated temperatures has been studied. In general, the products are the parent primary amine, propylene and resinous material. Some quinoline was formed from allylaniline at 700°. Allene was not a product of the pyrolysis. Mechanisms have been suggested and discussed.

The following new compounds have been prepared and characterized: diallyl-*p*-phenetidine, allyl-*p*-toluenesulfonanilide and *p*-toluenesulfone-*p*-phenetidide.

EVANSTON, ILLINOIS

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

# ROTENONE. X. CLEAVAGE OF DERRITOL AND ROTENOL

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

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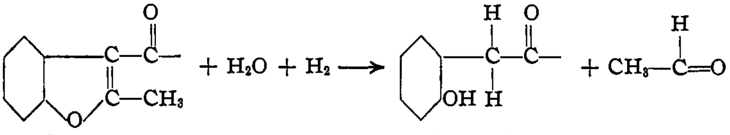
When rotenone, $C_{23}H_{22}O_6$, is boiled with zinc dust and potassium hydroxide in alcoholic solution, two products are obtained: derritol, a yellow phenol formed with the loss of two carbon atoms, and a white compound, rotenol,[1] which contains two hydrogen atoms more than rotenone and which exhibits the properties of an alcohol.

Butenandt[1] has advanced several theories to account for the formation of derritol of which the following mechanism is an example



Rotenone Derritol

Rotenol is assumed by the same author to be formed by the reduction of the carbonyl group of rotenone to a secondary alcohol group.

In previous articles[2,3] we have reported that several compounds derived

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[1] Butenandt, *Ann.*, **464**, 253 (1928).

[2] La Forge and Smith, THIS JOURNAL, **52**, 1091 (1930).

[3] La Forge and Smith, *ibid.*, **52**, 3603 (1930).

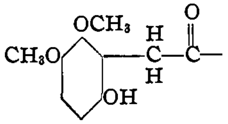
from dehydrorotenone are cleaved by hydrogen peroxide in alkaline solution to dibasic acids which contain the original two methoxy groups present in rotenone. Derric acid of formula $C_{12}H_{14}O_7$ was obtained from hydroxyrotenonic, as well as from dihydroxyrotenonic acids, while dehydrorotenonic acid gave the next lower homolog of derric acid, $C_{11}H_{12}O_7$, the latter acid being identical with the permanganate oxidation product of derric acid.

Both derritol and rotenol, as already reported,[4] yield acids on catalytic hydrogenation although in the case of derritol it is found convenient to methylate the phenol group in order to facilitate separation of the dihydroderritol and derritolic acid. In the case of rotenol the original double bond in the side chain of rotenone is also reduced during hydrogenation to the acid. The two resulting compounds, methylderritolic and dihydrorotenolic acids, are both well adapted to oxidation by the alkaline peroxide method and both yield interesting cleavage products.

Methylderritolic acid yields a monobasic trimethoxy acid of formula $C_{11}H_{14}O_5$ corresponding to a trimethoxyphenylacetic acid. Permanganate oxidation of this compound yields the next lower homolog, an acid of formula $C_{10}H_{12}O_5$, still containing the three methoxyl groups, and in all probability, a trimethoxybenzoic acid. Of the six theoretically possible compounds of this nature, four are known, but the properties of the compound obtained from derritol do not correspond to those of any of them. There remain the 2,3,5- and 2,3,6-trimethoxybenzoic acids of which the new compound most likely corresponds to the last-mentioned derivative. The choice between the two possibilities must be decided by synthesis of one or both of the missing members.

It follows from the facts so far established that the phenolic hydroxyl group in derritol arises from the indifferent oxygen atom in rotenone, that this group is attached to the same benzene nucleus as the methoxyl groups and that at least one carbon atom separates that nucleus from the carbon atom, probably the carbonyl group, at which cleavage takes place.

It seems probable therefore that derritol does in fact contain the grouping (A) as suggested by Butenandt.[1]



A

As mentioned above, dihydrorotenolic acid is easily cleaved by alkaline peroxide and in this case also a monocarboxylic acid is obtained in good yield.

The acid obtained from rotenol is represented by the formula $C_{12}H_{14}O_5$. It contains the original two methoxyl groups of rotenone, gives no test for a phenol and does not reduce Fehling's solution. The compound will be named netoric acid.

**Oxidation of Methylderritolic Acid with Hydrogen Peroxide.**—The procedure followed in carrying out this reaction was the same as that used for the preparation of derric

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[4] La Forge and Smith, THIS JOURNAL, **52**, 1088 (1930).

acid.[5] Two grams of methylderritolic acid[4] was dissolved in 25 cc. of 5% potassium hydroxide. The solution was warmed to 60° and 6 cc. of 30% hydrogen peroxide was added in small portions, after which the solution was boiled to remove any excess hydrogen peroxide. After cooling, the solution was made acid with dilute hydrochloric acid and extracted with ether. The ether solution was dried over anhydrous sodium sulfate and the ether evaporated. The residue crystallized at once. The oily by-products were removed by pressing the crystals between filter papers, after which the compound was recrystallized from water. The melting point was 93°; the yield, 0.7 g. Owing to the presence of water of crystallization, the substance was dried for analysis to constant weight at 110°.

*Anal.* Subs., 0.0740, 0.0772: $CO_2$, 0.1578, 0.1650; $H_2O$, 0.0411, 0.0423. Subs., 0.0218, 0.0143: AgI, 0.0676, 0.0455. Calcd. for $C_{11}H_{14}O_5$: C, 58.40; H, 6.15; $3CH_3O$: 41.4. Found: C, 58.16, 58.25; H, 6.16, 6.10; $CH_3O$, 40.96, 42.02. *Titration.* Subs., 0.0194: 0.905 cc. of $N/10$ KOH. Calcd. mol. wt.: 226. Found: 214.

Oxidation of Acid of Formula $C_{11}H_{14}O_5$ (Trimethoxyphenylacetic Acid).—Three-tenths of a gram of the acid was dissolved in 50 cc. of water containing an excess of potassium hydroxide and to the cold solution 0.45 g. of potassium permanganate dissolved in 50 cc. of water was added in small portions. When the purple color had disappeared, the solution was warmed on the steam-bath and filtered. After evaporation to a small volume the solution was acidified and extracted with ether and the ether solution dried over anhydrous sodium sulfate. After removal of the solvent the residue was distilled in a high vacuum. The distillate crystallized at once and was recrystallized from carbon tetrachloride. The melting point was 78–80°; the yield, 0.14 g. For analysis the substance was dried to constant weight at 110°.

*Anal.* Subs., 0.0737, 0.0766: $CO_2$, 0.1530, 0.1593; $H_2O$, 0.0404, 0.0434. Calcd. for $C_{10}H_{12}O_5$: C, 56.6; H, 5.66. Found: C, 56.62, 56.70; H, 6.09, 6.29. *Titration.* Subs., 0.0195: 1.76 cc. $N/20$ KOH. Calcd. mol. wt.: 212. Found: 221.

Amide.—One-half gram of the acid was dissolved in 12 cc. of dry benzene and 0.5 g. of phosphorus pentachloride was added. The solution was gently boiled until all of the hydrochloric acid was removed, then cooled in an ice-bath and dry ammonia gas passed into the solution. Water was then added and the benzene boiled off. The amide crystallized from the aqueous solution and was recrystallized from the same solvent. The melting point was 173° and the yield, 0.35 g. The compound was analyzed for nitrogen by the micro Kjeldahl method.

*Anal.* Subs., 0.0171: 0.76 $N/10$ HCl. Calcd. for $C_{10}H_{13}O_4N$: N, 6.63. Found: N, 6.46.

Oxidation of Dihydrorotenolic Acid.—The procedure followed in this reaction was also the same as that used for the preparation of derric acid.[5] Two grams of dihydrorotenolic acid[4] was dissolved in 25 cc. of 5% potassium hydroxide, the solution warmed to 60° and 6 cc. of 30% hydrogen peroxide was added in small portions. With each addition of hydrogen peroxide the solution was stirred until the precipitate which formed was dissolved. When the solution began to effervesce the stirring was discontinued. The reaction mixture was then boiled to remove excess peroxide and the small amount of separated resinous material extracted with ether. The solution was then acidified with dilute hydrochloric acid and extracted with ether. After drying over anhydrous sodium sulfate the ether was removed, leaving a sirupy residue which soon crystallized. The adhering oil was removed by pressing between filter papers. The compound was then recrystallized from water. The substance contained crystal water, and for an-

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[5] La Forge and Smith, This Journal, **52,** 2878 (1930).

alysis was dried to constant weight at 110°. The melting point was 91–92°. The yield was 0.5 g.

*Anal.* Subs., 0.0734, 0.0638: $H_2O$, 0.0055, 0.0044. Calcd. for $C_{12}H_{14}O_5{\cdot}H_2O$: $H_2O$, 7.04. Found: 7.4, 6.9. Subs., 0.0594, 0.0679; $CO_2$, 0.1318, 0.1515; $H_2O$, 0.0316, 0.0351. Subs., 0.0200, 0.0199: AgI, 0.0392, 0.0391. Calcd. for $C_{12}H_{14}O_5$: C, 60.50; H, 5.88; $2CH_3O$, 26.05. Found: C, 60.49, 60.84; H, 5.91, 5.74; $CH_3O$, 25.89, 25.95. *Titration.* Subs., 0.0201: 1.72 cc. *N*/20 KOH. Calcd. mol. wt.: 238. Found: 234. 0.1982 g. of subs. in 10.6 cc. of ethyl alcohol showed no appreciable rotation in a 2-dm. tube.

## Summary

Methylderritolic acid yields on alkaline peroxide oxidation a monocarboxylic acid of formula $C_{11}H_{14}O_5$ having the properties of a trimethoxyphenylacetic acid which yields the next lower homolog by permanganate oxidation. The new acid corresponds in its empirical formula to a trimethoxybenzoic acid but does not agree in its properties with any of the four known compounds of this type. It therefore probably corresponds to either the 2,3,5- or 2,3,6-derivative, both of which are unknown.

Dihydrorotenolic acid on peroxide oxidation yields a monocarboxylic acid of formula $C_{12}H_{14}O_5$ containing the two methoxyl groups of rotenol.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

# ON THE COURSE OF ADDITION OF SODIUM ENOL ALKYL MALONIC ESTERS TO ALPHA, BETA-UNSATURATED ESTERS

BY ARTHUR MICHAEL AND JOHN ROSS

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In the first account of the addition of sodium enol malonic ester to esters of $\alpha,\beta$-unsaturated acids[1] the reaction was expressed as though the parts of the addendum were Na and $-CH(COOEt)_2$

$$\begin{array}{ccc} \mathrm{RCH{=}CHCOOEt} & & \mathrm{RCHCHNaCOOEt} \\ + & \longrightarrow & \quad| \\ \mathrm{NaCH(COOEt)_2} & & \mathrm{HC(COOEt)_2} \end{array}$$

In agreement with this view, the many cases of $\alpha,\beta$-olefinic carboxylic esters that have since been examined by reaction with sodium enol malonic ester gave products that indicated that the malonic residue had united with the $\beta$-carbon atom. After the enol structure was assigned to the sodium derivative of malonic ester[2] the above reaction continued to be written as though the sodium atom migrated in the reaction.[3] This mecha-

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[1] Michael, *J. prakt. Chem.*, **35**, 349 (1887).

[2] Michael, *ibid.*, **37**, 496 (1889).

[3] Although usually written as though the sodium atom becomes attached to the $\alpha$-carbon atom of the unsaturated ester, attention had been called to the fact that the structure of such an addition compound would be unstable and would rearrange from the $-CHNaCOOEt$ to the $-CH{=}C(ONa)OEt$ form [Michael, *Ber.*, **33**, 3731 (1900)].