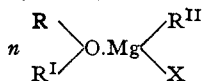


For the purpose of detecting minute traces of benzoic acid, an aqueous solution of copper propionate was employed. Preliminary tests had shown that this reagent was capable of giving a distinct precipitate in a neutral solution of benzoic acid at a dilution of 1 : 10,000. Since no precipitate was formed in the 30 cc. portion of neutral solution, benzoic acid, if produced at all in the reaction, must have been present in an amount less than 0.006 g.

### Conclusions.

1. The action of an alkyl (or aryl) halide upon magnesium in the presence of an ether results in the formation of certain addition products which may be represented by the general formula



2. The Grignard-Stadnikoff oxonium structure predicts that a given etherate may be prepared by either of two methods. Experimental data, however, indicate that the compounds formed are not identical—in fact all the evidence obtained is contrary to the theory of Stadnikoff.

3. It is unnecessary to assume any oxonium structure for the Grignard compounds in order to account for the decomposition products obtained with the common ethers (diethyl and phenyl-ethyl). If, however, the assumption of an oxonium structure is desired, the Baeyer-Villiger formula is to be preferred.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]  
**SOME TRANSFORMATIONS OF RICINOLEIC AND OLEIC ACIDS.**

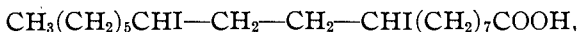
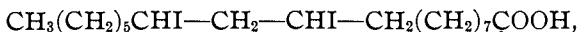
[SECOND PAPER.]

**ACTION OF MONOPOTASSIUM ANILIDE AND POTASSIUM PHENOLATE UPON DIBROMOHYDROXYSTEARIC AND DIBROMOSTEARIC ACID.**

By B. R. HONOVSKI.

Received March 5, 1914.

In my previous paper<sup>1</sup> it was shown that ricinoleic acid was changed to diiodostearic by the action of hydriodic acid. This acid upon reduction with nascent hydrogen is changed quantitatively to stearic acid. This reaction makes it certain that the iodine atoms in diiodostearic acid are not added to two neighboring carbon atoms:



otherwise, upon reduction with nascent hydrogen, an unsaturated acid would be obtained, similar to the dihalogen oleic, elaidic, fumaric, and maleic acids, which, upon reduction of their respective dihalogen-deriva-

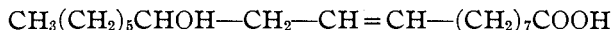
<sup>1</sup> *Ber.*, 42, 3339 (1909).

tives, give the original acids or their isomers. Consequently the formula:



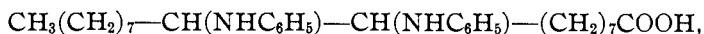
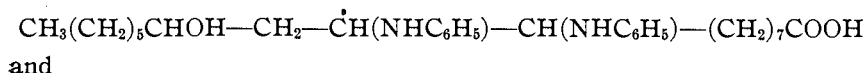
which has been proposed by Kraft<sup>1</sup> and based upon decomposition products of ricinoleic acid, cannot be accepted. An acid having hydroxyl and a double bond situated at two neighboring carbon atoms, should, upon action of HI, yield also a diiodo acid with neighboring iodine atoms and this would give an unsaturated acid upon reduction with nascent hydrogen.

The property which ricinoleic acid has of passing into stearic and dihydroxystearic acid with hydroxyl groups situated at two carbon atoms not adjacent, and into ricinostearic acid,  $\text{CH}_3(\text{CH}_2)_5-\text{CHOH}-\text{CH}_2-\text{C}\equiv\text{C}-(\text{CH}_2)_7\text{COOH}$ , which formula was given by Goldsobel,<sup>2</sup> and, on the other hand, the products of decomposition of ricinoleic acid such as oenanthol and undecylic acid obtained by destructive distillation or by oxidation with nitric acid<sup>3</sup> point to the fact that the constitution of ricinoleic acid may be expressed by the formula:



Desiring to obtain some data which would throw more light on this subject, and at the same time wishing to investigate the action of mono-substituted anilide and phenolate upon dihalogen hydroxy and dihalogen fatty acids, the following experiments were undertaken.

It was desired to obtain in the first case dianilidoderivatives of ricinoleic and oleic acid:



or, if such compounds are not capable of existence, certain definite products of their decomposition.

### Experimental.

*Dibromohydroxystearic acid.*—This acid was prepared in the usual way by adding 55 g. of Br to 100 g. of ricinoleic acid. After all of the acetic acid and ether were gone, a small amount of benzene (25–30 cc.) was added to dibromohydroxystearic acid and mixed thoroughly with 50 g. of dry and finely pulverized potassium carbonate. The mixture was kept on the water bath for a few hours, with occasional stirring and addition of benzene to prevent the product from passing into a solid mass.

For 150 g. of dibromohydroxystearic acid, 180 g. of monopotassium anilide were added (double the theoretical amount). This was prepared by gradually adding 52 g. of potassium to 200 g. of aniline, diluted with benzene to keep the product in liquid form.

<sup>1</sup> *Ber.*, 21, 2730 (1888).

<sup>2</sup> *Ibid.*, 27, 3121 (1894).

<sup>3</sup> *Ann.*, 120, 288 (1861); *Ber.*, 23, [2] 444 (1890); 24, 979 (1891).

The reaction between potassium and aniline takes place at the ordinary temperature, but after a while it is necessary to heat the mixture on the water bath and stir occasionally to distribute the melted potassium throughout the viscous liquid until all is dissolved.

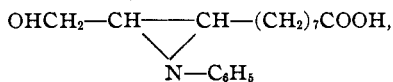
The casserol containing potassium anilide was placed in ice water and the potassium salt of dibromohydroxystearic acid was added in small portions and mixed thoroughly. After standing for 2-3 hours at ordinary temperature, the mixture was kept on the water bath for 12-15 hours with frequent stirring, and after all of the benzene was gone the product was placed in a porcelain dish, water was added and the mixture was brought to boiling. While still hot, the product was decomposed by adding hydrochloric acid and boiling for half an hour. The tarry oil, which solidifies on cooling, was removed from the surface and dissolved in ligroin. The solution was kept on the water bath and stirred with a glass rod to help the separation of the tarry matter which solidifies on the bottom. The liquid was poured to another beaker, which was kept for a while on the water bath until the ligroin solution became clear. In this way most of the tarry matter was separated. Then the ligroin was distilled off and the product was dissolved in alcohol and boiled with some excess of dry sodium carbonate and filtered very slowly into a solution of barium chloride with constant stirring. After the precipitation was completed, the clear liquid was poured off, if the precipitate sticks to the walls of the dish, or filtered if the precipitate was flocculent, and thoroughly dried. The dry precipitate was placed in a flask and digested with ether for a few days at the ordinary temperature, occasionally shaking. The ether solution was filtered off and digestion was repeated for 1-2 days. The ether was then filtered off and the residue washed on the filter with ether and decomposed by boiling with dilute hydrochloric acid. The fatty product which solidifies on the surface was removed, dried and dissolved in ligroin. After a few crystallizations from ligroin containing a little ether the product was further purified by boiling its alcoholic solution with animal charcoal for 20 hours. For further purification, the alcoholic solution was saturated with dry sodium carbonate and precipitated with barium chloride. The barium salt was recrystallized from boiling water, by adding salt in excess to water (3-4 liters), boiling for one-half hour and filtering hot.

By this method all other fatty acids, such as palmitic, stearic and some derivatives of oleic acid, were separated as insoluble in water. For the above reason the purification of ricinoleic acid by means of the lead salt can be avoided. The bulk of the solid acids can be separated by cooling ricinoleic acid below room temperature and filtering off.

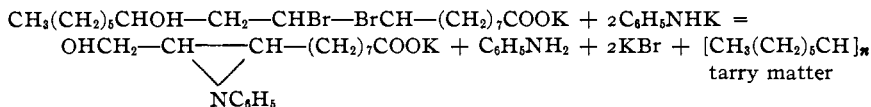
The acid, which was obtained from the barium salt and recrystallized from ligroin and ether, crystallizes in shining leaves, which melt at  $57-58^{\circ}$ .

It is soluble in all commonly used solvents and sparingly in hot water. Yield, about 35% theoretical.

Analyses of this substance gave results corresponding to the formula:



which shows that one molecule of monopotassium anilide replaces both bromine atoms situated at the neighboring carbon atoms. The hydroxyl group of dibromostearic acid is shifted toward the carboxyl group and the molecule of hydroxy dibromostearic acid splits up, giving 11-hydroxy-9,10-anilido undecylic acid,



where both hydrogen atoms of the amino group are replaced, as follows from the reaction with nitrous acid, which has no effect on hydroxyanilido-undecylic acid:

Samples of this acid gave the following results on combustion with copper oxide and copper spiral:

0.2165 and 0.2210 g. subs. gave C = 69.83, 69.68; H = 8.85, 8.92; calc. for C<sub>17</sub>H<sub>28</sub>NO<sub>3</sub>, C = 70.10 and H = 8.59

The amount of nitrogen was determined by the Kjeldahl method:

0.3630, 0.4350 g.; N, 4.54, 4.41; calc. for C<sub>17</sub>H<sub>28</sub>NO<sub>3</sub>, N = 4.81

The barium and silver salt were prepared by saturating an alcoholic solution of the acid with dry sodium carbonate and precipitating the filtrate with barium chloride and silver nitrate.

Both salts are soluble in water and alcohol.

0.3290 g. of the Ba salt gave 18.76% Ba and 0.4130 g. gave 19.09% Ba; calc. 19.10% Ba.

0.6810 g. Ag salt gave 27.01% Ag, and 0.3085 Ag salt gave 26.90% Ag; calc. 27.13% Ag.

*Acetic Ester of Hydroxyanilido Undecylic acid.*—The presence of the hydroxyl group in the acid was proved by obtaining the acetic ester of the acid by heating the acid with ten times the amount of acetic anhydride, required by theory in a sealed tube at 110° during 8 hours.

It is a colorless viscous liquid which saponifies with caustic alkali to the hydroxy acid. The saponification was done in alcoholic solution, using 3–4 times the quantity of metallic sodium necessary to neutralize the products of saponification. The blank sample was run at the same time, using alcohol from the same bottle.

1.1395 of the ester required 0.1568 Na = 13.76% Na.

1.2535 of the ester required 0.1714 Na = 13.67% Na.

Calculated for (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>Na + C<sub>17</sub>H<sub>28</sub>NO<sub>3</sub>Na) 13.81% Na.

*Lactone of Hydroxyanilidoundecydic Acid.*—Hydroxyanilidoundecydic acid, on standing for a few weeks, gradually becomes liquid and by loss of one mol of water is converted to the lactone.<sup>1</sup> The same change takes place upon warming the acid with dilute (1-2) H<sub>2</sub>SO<sub>4</sub> for a few hours on the water bath. The lactone is easily saponified to the hydroxy acid.

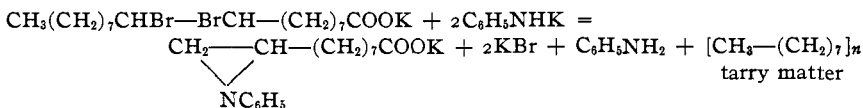
0.2315 and 0.2420 g. lactone gave 74.38 and 74.46% C; and 8.93 and 8.70% H. Calc. for C<sub>17</sub>H<sub>23</sub>NO<sub>2</sub>, C, 74.72; H, 8.42.

*Dibromohydroxyanilidoundecydic Acid.*—This was prepared in the usual way, using dry ether and glacial acetic acid as a solvent. The amount of bromine was added in the proportion of about three atoms of bromine to one mol of the acid. During bromination and on standing for twelve hours, as well as during evaporation of the solvents on the water bath, no evolution of hydrobromic acid was noticed. The dibromohydroxyanilido acid is a viscous yellow liquid which, after a few months of keeping in the desiccator, decomposes slightly. Upon reduction with zinc dust in glacial acetic acid, the compound was changed to the original acid. This reaction and the ability to combine with bromine without evolution of hydrobromic acid brings us to the conclusion that the reaction with Br is a simple additive one.

0.2965 g. of the bromide gave 35.28 and 0.3120 g. of the bromide gave 35.32% Br. Calc. for C<sub>17</sub>H<sub>26</sub>Br<sub>2</sub>NO<sub>3</sub>, 35.47% Br.

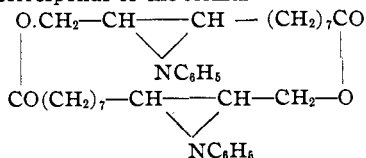
*9-10-Anilidodecylic Acid*,  $\begin{array}{c} \text{CH}_2 \text{---} \text{CH} \text{---} (\text{CH}_2)_7 \text{COOH} \\ \diagdown \quad \diagup \\ \text{NC}_6\text{H}_5 \end{array}$  was obtained in

exactly the same manner as hydroxyanilidoundecydic acid. Dibromostearic acid, which was prepared by adding bromine to oleic acid, was changed to the potassium salt as described above and mixed with double amount of monopotassium anilide.



The separation of the acid from the tarry matter is carried out in the same order as described above, but the purification of the acid by crystallizing its barium salt from hot water was omitted. 9,10-Anilidodecylic acid is a white amorphous powder, which melts at 54-55°, is soluble in all commonly used solvents, but not in water, and does not combine with bromine.

<sup>1</sup> The analysis also corresponds to the formula of the lactide



Analyses of this acid gave the following data:

0.2030 and 0.1880 g. acid gave C = 73.30 and 73.41; H, 9.07, 8.95. Calc. for  $C_{16}H_{23}NO_2$ , C = 73.56 and H = 8.81; 0.4020 and 0.4240 g. subs. gave (Kjeldahl method) N = 5.15 and 5.18; calc. N = 5.36.

The barium and silver salts were prepared by precipitating the sodium salt of the acid with  $BaCl_2$  and  $AgNO_3$  solution. Both salts are insoluble in water.

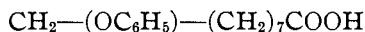
0.1995 g. of silver salt gave 29.32% Ag; 0.2570 of barium salt gave 20.59% Ba; calc. for  $C_{17}H_{22}NO_2Ag$ , 29.34% Ag;  $(C_{17}H_{22}NO_2)_2Ba$ , 20.85% Ba.

The difference in chemical properties between hydroxyanilidoundecydic acid and anilidodecylic acid is the readiness of the first acid to form a dibromoderivative. The second acid does not combine with bromine.

On applying a 1 or 2% solution of potassium permanganate in order to change the hydroxyanilido acid to the trihydroxy acid, it was found that some decomposition took place, but most of the acid was recovered unchanged. This reaction gives a certain proof, that hydroxyanilidoundecydic acid does not possess a double bond in the open chain, and consequently the two bromine atoms are situated in the benzene ring.

*Phenoxy Derivatives of Oleic Acid* were obtained by the action of phenol on dibromostearic acid in the presence of potassium carbonate. Dibromostearic acid was mixed with 180 g. of pulverized potassium carbonate and 150 g. of phenol. The mixture was heated for twelve hours at 105–108° and frequently stirred. Then water was added and the product was salted out as a viscous mass and warmed for some time with a solution of barium chloride. The water was poured off and the precipitate of barium salt, a viscous mass, was left on the same dish to dry and then transferred to the flask and boiled for a while with alcohol in order to take up the moisture and some phenol remaining. After cooling the alcohol was poured off and ether was added to extract the oily decomposition products of dibromostearic acid. In this ethereal solution was found also a considerable quantity of unchanged dibromostearic acid.

The barium salt remaining undissolved in ether was decomposed by boiling with dilute hydrochloric acid and the product was removed after cooling and dissolved in ligroin on the water bath. A small part of this product was left undissolved in ligroin and was filtered off. The first part of this product, which was readily soluble in ligroin, was crystallized out of ligroin and alcohol. It is a white crystalline powder with characteristic odor which melts at 58–59° and according to analysis corresponds to the formula:



0.1985 g. and 0.2050 g. subs. gave C = 71.63 and 71.56; H = 9.11 and 9.21; calc. for  $C_{15}H_{22}O_3$ , C = 72.00; H = 8.80.

The barium and silver salts were prepared by precipitation of sodium salt with  $BaCl_2$  and  $AgNO_3$ .

0.4090 g. of the Ag salt gave 30.19% Ag; 0.4670 g. of the Ag salt gave 30.08% Ag; calc. for  $C_{15}H_{21}O_3Ag$ , Ag = 30.25; 0.3315 and 0.2845 g. of the Ba salt gave 21.50 and 21.42% Ba; calc. for  $(C_{15}H_{21}O_3)_2Ba$ , Ba = 21.59.

The bromide was prepared by adding two atoms of bromine to one mol of the acid. It is a crystalline monobromosubstituted phenoxyacid.

0.1440 and 0.1275 of the bromide gave 24.18 and 24.09% Br; calc. for  $C_{15}H_{21}BrO_3$ , Br = 24.31.

*Condensation Product.*—The second part of this product, obtained in very small quantity (about 1 g.), which is not soluble in ligroin but readily in alcohol, and very readily in acetic acid, is a white crystalline powder which melts at 96–97°.

0.4615 g. of its silver salt gave 11.70% Ag and 0.1790 g. of the bromide gave 0.0875 AgBr = 20.79% Br.

Judging from these data, this acid is probably a condensation product of the decomposition products of the phenoxyacids and corresponds to the formula  $C_{60}H_{94}O_6$ .— $3CH_3(CH_2)_7CH_2(C_6H_5O) + CH_2(C_6H_5O)(CH_2)_7COOH$ —for which the calculated amount of silver is 11.88% and of bromine calculated for a tribromosubstituted derivative is 20.87%.

The next experiment for the preparation of phenoxyacids was carried out in the same manner as described above, but the temperature was raised to 140° and kept there during twenty hours. This product crystallizes from alcohol in large aggregates consisting of long needles; m. p. 54–55°. The data obtained by analyzing this acid closely correspond to those of the first acid  $CH_2-(C_6H_5O)-(CH_2)_7COOH$  as follows:

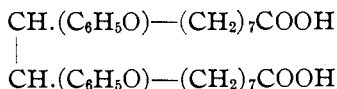
0.2005 and 0.2120 g. of the acid gave C = 72.06 and 72.13; H = 8.67 and 8.72; 0.1035 g. of the barium salt gave 21.53% Ba; 0.3160 g. of silver salt gave 0.0955 Ag = 30.22% Ag.

The bromide is a white crystalline substance.

0.1470 and 0.1210 g. of the bromide gave 24.02 and 24.06% Br.

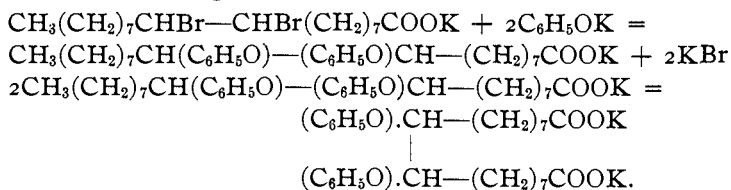
The identity in composition of these two acids established by analyses, and the difference in physical properties points out that the last acid is either isomeric with the first acid or its molecule consists of two molecules of the first acid. Consequently it was necessary to determine the molecular weight of these two acids.

The determination was done by using the Eijkmann cryoscopic apparatus, using as a solvent glacial acetic acid. In spite of care to prevent the solvent from taking up moisture, a few determinations of different concentration of the solutions gave a depression of melting point corresponding to a molecular weight of the first acid  $CH_2-(C_6H_5O)-(CH_2)_7COOH$ , 272–279 against 250; and 516–526 against 498 for

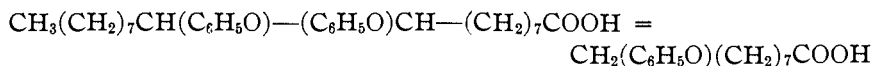


The increased concentration of the solution gives an increase in molecular weight.

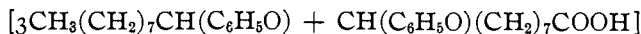
The data obtained differ greatly from those obtained by analyses and the difference between the values of each one of the above acids is too considerable to admit assigning a value to any one of these determinations by themselves. In comparison with each other, however, they show that the molecular weight of the second acid is much greater (almost double the first acid). Taking into consideration that these two acids are formed under different conditions in temperature and were not found together in any proportions in the same experiment and the difference in crystalline form and molecular weight, it will be necessary to admit that the second of these acids is a condensation product of the first and its formula will be according to the formation:



Under the same conditions, but lower temperature, two other acids are formed:



and



The investigation is being continued.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]

## INTERPRETATIONS OF SOME STEREOCHEMICAL PROBLEMS IN TERMS OF THE ELECTRONIC CONCEPTION OF POSITIVE AND NEGATIVE VALENCES.

### II. HALOGEN SUBSTITUTION IN THE BENZENE NUCLEUS AND IN THE SIDE CHAIN.

By HARRY SHIPLEY FRY.

Received March 16, 1914.

The present paper, the second of a series<sup>1</sup> relating particularly to the interpretations of some stereochemical problems, is an extension of the principles which have been presented, applied, and discussed in previous papers.<sup>2</sup> The subject matter of this paper, halogen substitution in the

<sup>1</sup> Fry, *THIS JOURNAL*, 36, 248 (1914).

<sup>2</sup> Some of the earlier papers dealt with problems relating to chemical constitution from the standpoint of electronic formulas and chemical properties. Fry, *THIS*