[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND CLARKE UNIVERSITY.]

THE DECOMPOSITION OF NITROSO COMPOUNDS. II.

BY WILLIAM A. NOYES AND JAMES A. COSS.

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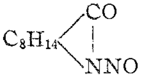
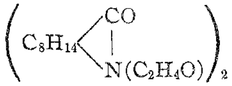
The work described in this paper was carried out partly at the University of Illinois and partly at Clarke University. It was mostly completed before the closely related work of A. Oppe[1] appeared, but for various reasons publication was delayed. We wish to express our indebtedness to Professor M. A. Rosanoff for the use of the chemical laboratory of Clarke University, in which the latter part of the work was done, and for valuable suggestions made in difficult parts of the investigation.

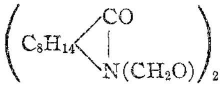
Some years ago Taveau[2] and one of us found that when the nitroso derivative of the anhydride of amino-lauronic acid,



moistened with ethyl alcohol, is treated with a 10% solution of sodium hydroxide a compound is formed to which the semi-empirical formula,

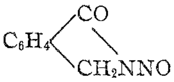


was given. With methyl alcohol a similar compound,



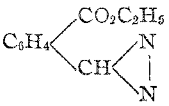
is formed.

A study of the decomposition of nitroso-phthalimidine,



was undertaken in the hope of securing further light on the reaction. It was soon found that when an alcoholic solution of this compound is treated with a small amount of sodium hydroxide the ethyl ester of ethoxy-toluic acid, $C_2H_5O_2.CC_6H_4CH_2OC_2H_5$, is formed.

Further study led to the discovery that at a low temperature nitroso-phthalimidine gives diazo-toluic ester,



when treated with alcoholic sodium hydroxide. When this red, diazo

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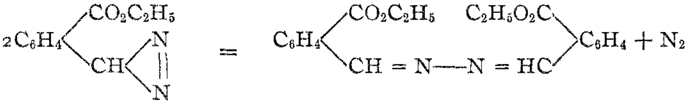
[1] *Ber.*, **46**, 1095 (1913).

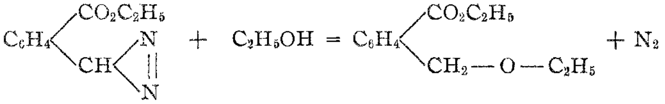
[2] *Am. Chem. J.*, **32**, 290 (1904).

compound is allowed to stand in an alcoholic solution it changes slowly to the *bis*-hydrazone of phthaldehydic ester:



$$2C_6H_4\left<\begin{array}{l}CO_2C_2H_5\\ CH\left<\begin{array}{c}N\\ \|\\ N\end{array}\right.\end{array}\right. = C_6H_4\left<\begin{array}{l}CO_2C_2H_5 \quad C_2H_5O_2C\\ CH = N - N = HC\end{array}\right>C_6H_4 + N_2$$

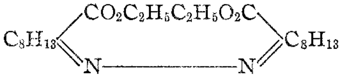
If a solution of the diazo compound in absolute alcohol is boiled, the ethyl ester of ethoxy-toluic acid is formed:



$$C_6H_4\left<\begin{array}{l}CO_2C_2H_5\\ CH\left<\begin{array}{c}N\\ \|\\ N\end{array}\right.\end{array}\right. + C_2H_5OH = C_6H_4\left<\begin{array}{l}CO_2C_2H_5\\ CH_2 - O - C_2H_5\end{array}\right. + N_2$$

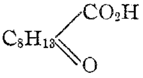
This is, of course, similar to the formation of anisole and other ethers by the action of diazomethane on phenol and other alcohols.

In the light of these results it is evident that the compound referred to at the beginning of this paper is the *bis*-hydrazone of camphononic ester,



$$C_8H_{13}\left<\begin{array}{l}CO_2C_2H_5C_2H_5O_2C\\ N \text{———————} N\end{array}\right>C_8H_{13}$$

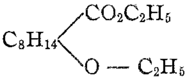
This conclusion was confirmed by hydrolyzing the compound by heating it with hydrochloric acid. This gave camphononic acid,



$$C_8H_{13}\left<\begin{array}{l}CO_2H\\ O\end{array}\right.$$

and hydrazine hydrochloride.

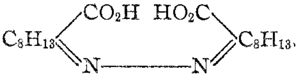
The ether ester of hydroxy-lauronic acid,



$$C_8H_{14}\left<\begin{array}{l}CO_2C_2H_5\\ O - C_2H_5\end{array}\right.$$

analogous to the ether ester of hydroxy-toluic acid spoken of above, was also obtained.

The compound spoken of as possibly an azo compound at the close of Taveau's[1] paper was, of course, the *bis*-hydrazone of camphononic acid,



$$C_8H_{13}\left<\begin{array}{l}CO_2H \quad HO_2C\\ N \text{————} N\end{array}\right>C_8H_{13}.$$

This differs by only 2 hydrogen atoms from the diazo formula suggested and the analytical results for nitrogen and for titration with alkali agree better with the *bis*-hydrazone formula than with the other.

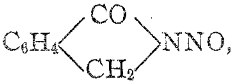
So far as we can discover, no one else has observed the formation of a *bis*-hydrazone from a diazo compound in the manner described in this paper. There seems to be good reason to expect that the reaction may occur in many other similar cases.

[1] *Am. Chem. J.*, 32, 293 (1904).

Experimental Part.

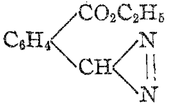
Phthalimide was prepared by a modification of Dunlop's[1] method, using ammonium carbonate in place of urea. Twenty-five g. of phthalic anhydride was mixed with an equal weight of ammonium carbonate and the powdered mixture was heated in a long-necked flask till the whole was in a state of quiet fusion at 300°. After cooling and crystallizing from water, 22 g. of phthalimide was obtained.

Phthalimidine and its Nitroso Derivative,



$C_6H_4<\begin{matrix}CO\\CH_2\end{matrix}>NNO$, were prepared by the method of Graebe,[2] but the method of Oppe[3] is probably better.

Diazo Compound,

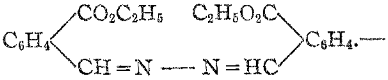


$C_6H_4<\begin{matrix}CO_2C_2H_5\\CH<\begin{matrix}N\\ \|\\ N\end{matrix}\end{matrix}$.—To 8 g. of nitroso-phthalimidine dissolved in 30 cc. of ethyl alcohol and cooled with ice and salt, 2 g. of sodium hydroxide dissolved in 20 cc. of alcohol was slowly added. Some nitrogen was evolved and the solution became of a bright red color. After standing in the freezing mixture for an hour large red crystals were formed; these were separated and recrystallized from alcohol. The compound melts at 39°.

Calc. for $C_{10}H_{10}O_2N_2$: C, 63.16; H, 5.26; N, 14.73. Found: C, 62.78, 62.84; H, 5.25, 5.23; N, 15.50, 15.49.

A molecular weight determination by the cryoscopic method gave the following results: 0.2168 g. dissolved in 22.23 g. of benzene gave a depression of 0.253°, and 0.3444 g. gave a depression of 0.416°. These results correspond to a molecular weight of 188 and 182, respectively. Calc. for $C_{10}H_{10}N_2O_2$ = 190.

***Bis*-hydrazone of Phthaldehydic Acid,**



$C_6H_4<\begin{matrix}CO_2C_2H_5 & & C_2H_5O_2C\\ CH=N & — & N=HC\end{matrix}>C_6H_4$.—When the diazo compound is allowed to stand in an alcoholic solution, the red color gradually disappears and in 2 or 3 days a yellow compound separates from the solution. When a new solution is gently warmed nitrogen is evolved and the color changes to pale yellow. On cooling and seeding with the yellow crystals, almost the theoretical yield of the *bis*-hydrazone is obtained. It melts at 145°.

Calc. for $C_{20}H_{20}O_4N_2$: C, 68.18; H, 5.68; N, 7.95. Found: C, 68.20, H, 6.03; N, 8.07.

By the cryoscopic method, 0.1120 g. in 44 g. of benzene gave a de-

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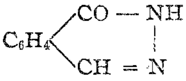
[1] *Am. Chem. J.*, **18**, 332 (1896).

[2] *Ann. Chem.*, **247**, 288 (1888).

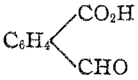
[3] *Ber.*, **46**, 1099 (1913).

pression of 0.38°, which corresponds to a molecular weight of 324. The molecular weight for the formula $C_{20}H_{20}O_4N_2$ is 352.

Phthalazone and Phthaldehydic Acid.—When the *bis*-hydrazone is heated with conc. hydrochloric acid in a sealed tube at 130° for an hour, phthalazone,



and phthaldehydic acid,



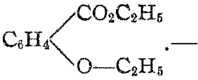
$$C_6H_4\begin{cases}CO_2H\\CHO\end{cases}$$

are formed. The phthalazone melted at 183°, and gave, by analysis:

Calc. for $C_8H_6N_2O$: C, 68.75; H, 4.11; N, 19.18. Found: C, 65.62, 65.71; H, 4.27, 4.24; N, 19.30, 19.16.

The solution of phthaldehydic acid reduced Fehling's solution and gave a deep red color when warmed with ferric chloride and sulfuric acid.

The *bis*-hydrazon, melting at 145°, was also prepared by adding hydrazine hydrate to a solution of phthaldehydic acid.

Ether-ester,  $C_6H_4\begin{cases}CO_2C_2H_5\\O—C_2H_5\end{cases}$.—When a solution of the red diazo compound in absolute alcohol was boiled nitrogen was rapidly evolved and in half an hour the solution became colorless. The alcohol was distilled off and the oily liquid which remained was distilled under diminished pressure. The major portion came over at 160°, under a pressure of 20 mm. This distillate contained some phthalide, which was removed by washing it with a solution of potassium hydroxide. As it was found difficult to purify the oil, it was saponified by boiling it with an alcoholic solution of potassium hydroxide. After evaporating away the alcohol, the acid was precipitated with hydrochloric acid. It was recrystallized 3 times from hot water, dried and re-esterified by heating it for 4 hours with absolute alcohol containing 5% of hydrochloric acid. The alcohol was distilled off, the residue washed with water, taken up with ether, and the ether distilled. The residue was dried over calcium chloride and distilled under diminished pressure. The clear oily compound had a pleasant, fruity odor.

Calc. for $C_9H_{14}O_3$: C, 69.23; H, 6.79. Found: C, 68.60; H, 7.66.

Molecular weight determinations by the cryoscopic method with benzene as the solvent gave unsatisfactory results, probably due to association. With glacial acetic acid, 0.742 g., in 28 g. of the acid, gave a depression of 0.49°; 0.4300 g. in 12.89 g. gave a depression of 0.63°. These results correspond to molecular weights of 210 and 205, respectively. The theoretical value is 208. n^{25} 1.49556, and d^{25}_{25} 1.059. This gives a molar refraction of 57.39 by the formula $\frac{M(n - 1)}{(n + 2)d}$. Bruhl's values for atomic refractions give the calculated value, 57.46, for the molar refraction.

It is noteworthy that in the method of preparation described the *bis*-hydrazone as well as the diazo compound is transformed to the ether ester.[1]

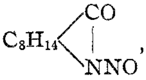
A portion of the ether ester was decomposed and reduced to *o*-toluic acid by heating it with red phosphorus and hydriodic acid. The latter melted at 104°. 0.0845 g. of the acid required 6.9 cc. of 0.1 *N* sodium hydroxide solution for neutralization. The calculated amount is 6.2 cc. The result is not satisfactory, but it shows that the acid was monobasic.

0.5 g. of the ether acid was oxidized in a sealed tube with nitric acid. The product, after recrystallizing from hot water, melted at 207° and was converted to the anhydride. The latter, after cooling, melted at 128°.

Ethoxy Acid.—This was prepared as described above. It melts at 84.5°.

Calc. for $C_9H_{10}O_3$: C, 66.67; H, 6.72. Found: C, 66.40; H, 6.67.

Subs., 1.1295; 62.94 cc. of 0.1 *N* sodium hydroxide soln. Calc., 62.73.

Derivatives of Amino-lauronic Acid.—When 20 g. of the nitroso derivative of the anhydride of amino-lauronic acid,  $C_8H_{14}\!\left<\begin{matrix}CO\\ |\\ NNO\end{matrix}\right.$, was added in small portions to a cooled solution of 2.5 g. of sodium in 75 cc. of absolute alcohol, a bright red color appeared, indicating the formation of the diazo compound. This did not separate, however, as in the case of the derivative of phthalimidine described above. After 3 hours the red color had disappeared and given place to a yellow. The straw-colored solution was diluted with water and extracted with ether. The ethereal solution was washed with water to remove the alcohol, dried with sodium sulfate and the ether distilled. From the residue, by cooling with a freezing mixture, crystals melting at 104° were obtained. These were evidently identical with the compound described by Noyes and Taveau.[2]

From analogy this compound is evidently the *bis*-hydrazone of camphononic acid, corresponding to the *bis*-hydrazone of phthaldehyde acid obtained from phthalimidine. In order to test this interpretation more positively, the compound was hydrolyzed by heating it in a sealed tube

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[1] Staudinger and Mäckling (*Ber.*, **49**, 1973 (1916)) report the formation of the methyl ether ester together with phthalide when the diazo ester is allowed to stand in moist air. They do not seem to have noticed that this is similar to the formation of ethers and esters by the use of diazomethane, and they do not report the *bis*-hydrazone which we have found. We have noticed the same poisonous, eczema producing quality of the nitroso compound which they found so troublesome.

[2] *Am. Chem. J.*, **32**, 291 (1904).

with 20% hydrochloric acid at 150–160° for 3 hours. This gave camphononic acid, which was identified, after recrystallizing it from water, by its melting point of 230–231°. When mixed with camphononic acid the mixture melted at 232°. In a benzene solution the specific rotation at 22° was 23.2°, while that of a sample of camphononic acid was 23.5°. Potter and Noyes[1] give the rotation as 17.8° at 27.5°.

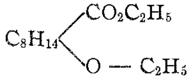
By evaporating the solution from which the camphononic acid had been separated, hydrazine hydrochloride was obtained. The chlorine in this was determined as silver chloride, the hydrazine by titration with potassium permaganate after adding silver sulfate. The analysis gave:

Subs., 0.0315; AgCl, 0.0880. Subs., 0.0665; N_2H_4, 0.0216.

Calc. for $N_2H_4.2HCl$: Cl, 67.60; N_2H_4, 30.50. Found: Cl, 69.10; N_2H_4, 32.43.

The results found are not satisfactory, but not enough material was available for us to repeat the analysis.

Ether-ester.—The mother liquors from which the *bis*-hydrazone was crystallized were distilled under a pressure of 3 mm. Most of the material distilled at 113–115°.

Calc. for 
$C_8H_{14}\left<\begin{array}{l}CO_2C_2H_5\\ O-C_2H_5\end{array}\right.$: C, 68.42; H, 10.52. Found: C, 68.14; H, 10.36.

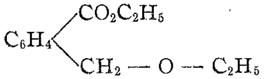
Summary.

1. Phthalimide can be prepared easily and in good yield by heating a mixture of phthalic anhydride with an equal weight of ammonium carbonate.

2. Nitroso-phthalimidine is converted into a diazo compound when a suspension of it in cold absolute alcohol is treated with sodium ethylate. The yield is poor and Oppe's method is probably better.

3. When a solution of the red diazo compound in alcohol is warmed gently it is converted to the *bis*-hydrazone of phthaldehydic acid.

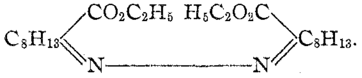
4. When a solution of either the diazo compound or of the *bis*-hydrazone in alcohol is boiled, the ether-ester of hydroxy-toluic acid,



$$C_6H_4\left<\begin{array}{l}CO_2C_2H_5\\ CH_2-O-C_2H_5\end{array}\right.$$

is formed.

5. In the light of these results, the compound discovered by Noyes and Taveau was undoubtedly the *bis*-hydrazone of the ester of camphononic acid,



$$C_8H_{13}\left<\begin{array}{lcr}CO_2C_2H_5 & & H_5C_2O_2C\\ N & \text{———————} & N\end{array}\right>C_8H_{13}.$$

6. In confirmation of this formula this compound was hydrolyzed to camphononic acid and hydrazine.

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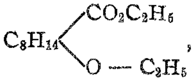
[1] This Journal, 34, 67 (1912).

7. The ether acid of camphonolic acid,



$$C_8H_{14}\left\langle\begin{matrix}CO_2C_2H_5\\O-C_2H_5\end{matrix}\right.,$$

is formed when the *bis*-hydrazone is boiled with alcohol.

URBANA, ILL., AND SIOUX CITY, IA.

NOTES.

Oil of Rubieva Multifida.—A specimen of the essential oil of *Rubieva Multifida*, distilled experimentally by the W. J. Bush Citrus Products Company, at National City, California, from the wild plants growing in the state, was examined.

The oil is light yellow in color and has an odor suggesting anise and terpenes. $d_{25^\circ}^{25^\circ} = 0.8542$. $[\alpha]_D = +35.75^\circ$ (100 mm. tube).

On the first distillation about 60% comes over at 37–40° (under 3 mm. pressure). On repeated refractionation, about 85% of the oil was found to consist of a terpene fraction which, after rectifying over sodium, boils at 169–171° (under atmospheric pressure). $d_{20^\circ}^{20^\circ} = 0.8507$, $[\alpha]_D = +46.4^\circ$ (100 mm. tube).

The terpene fraction polymerizes rapidly on boiling at atmopsheric pressure, has an odor resembling that of phellandrene, and yields a nitrosite melting at 103–104°. Hence it consists largely of β-phellandrene.

From the higher boiling portion of the oil anethole was separated. A resinous residue, probably polymerized phellandrene, was left on distillation.

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In connection with the writer's recent paper on "The Effect of Surface Oxidation on Some Metallic Catalysts,"[1] his attention has been called to Michael Faraday's work[2] on the same subject. The investigation of Faraday led to conclusions practically identical with those numbered 1 and 4 in the writer's summary so far as platinum is concerned, namely, that its activity is increased by surface oxidation and is not much affected by reduction. Faraday also studied other phases of the problem, including the effect of the presence of small amounts of various gases. His paper, however, does not deal with the subjects leading to the writer's other conclusions.

FRANK F. RUPERT.

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[1] THIS JOURNAL, **42,** 402 (1920).

[2] *Trans. Roy. Soc.* (*London*), **124,** 55 (1834); "Experimental Researches in Electricity," **1,** 165.