vent radiation. Such an arrangement brings the heat in contact with all sides of the inner chamber, which is necessary to secure a constant temperature. A piece of asbestos board one-fourth inch in thickness and the exact size of the oven was placed on the bottom shelf and served not only as an excellent support for the receptacles, but prevented any flame from reaching the inside. Strips of sheet iron 1 x 1/16 inch were used to support the bottom shelf firmly and keep the inside lining in place.

This air-bath has proven invaluable for moisture determinations, as a constant temperature is easily maintained. For temperatures up to 110° a Fletcher's evaporating burner is used, and for higher temperatures a Fletcher's solid flame boiling burner.

The above described air-bath has been in use in the laboratory for some time and has given perfect satisfaction. It can be recommended not only on account of its efficiency, but also because of its low cost.

Numerous tests were made with thermometers placed at different points to determine the distribution of heat in various parts of the oven. Very little variation occurs, the difference being only about one degree between the hottest and coolest parts of the oven. The field registering the greatest heat is about 1 inch above the lower shelf, and that giving the lowest heat is about 2 inches below the center of the top of the oven, opposite the ventilators.

UNIVERSITY OF ILLINOIS, URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

ON ETHYL PYROMUCYLACETATE. (SECOND PAPER). 3-FURYL-5-PYRAZOLONE.

BY HENRY A. TORREY AND J. E. ZANETTI.

Received June 19, 1908.

1-Phenyl-3-furyl-5-pyrazolone, formed by the action of phenyl hydrazine on ethyl pyromucylacetate, and several of its derivatives, were described in a previous paper[1]. 3-Furyl-5-pyrazolone, obtained by the action of hydrazine itself on the same ester, forms the subject of the present paper.

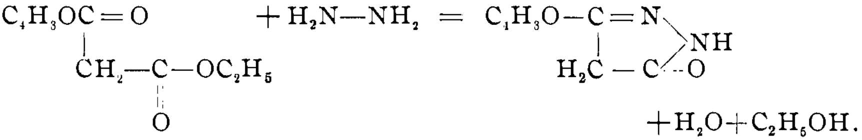
It is possible that this reaction takes place in two stages, as in the case of phenylhydrazine and acetacetic ester[2] but neither in the action of hydrazine hydrochloride and sodium acetate nor in the more direct action of hydrazine hydrate was an intermediate product isolated.

The constitution of the pyrazolone as a 3-furyl-5-pyrazolone follows from its method of formation

---

[1] *Am. Chem. J.*, **36,** 539.

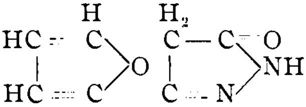
[2] Nef, *Ann.*, **266,** 70.



The melting point, 223°, falls, as might be expected, between those of 3-methyl-5-pyrazolone, 215°[1] and 3-phenyl-5-pyrazolone, 236°.[2]

That the pyrazolone group is attached to the furane ring in the α position is also evident from its formation from ethyl pyromucylacetate.

The furyl pyrazolone gives the characteristic reactions of compounds of this class yielding a monacetyl and a diacetyl derivative and a condensation product with benzaldehyde. With sodium nitrite and hydrochloric acid it gives a red nitroso compound, an indication, according to Michaelis,[3] of a 5-pyrazolone. By the action of phenyl isocyanate a condensation product was obtained in the formation of which the imide group is doubtless concerned, giving a pyrazolone-phenyl-urea.

3-Furyl-5-pyrazolone,  .—This compound was made by heating a dilute alcohol solution of ethyl pyromucylacetate with hydrazine sulphate and sodium acetate in molecular proportions. It could also be obtained by heating the ester with a solution of hydrazine hydrate, neutralizing with acetic acid and salting out with sodium acetate. The pyrazolone separates out as a brown crystalline powder which can be obtained perfectly white in color by washing with ether and crystallizing from dilute methyl alcohol.

Calculated for $C_7H_6N_2O_2$: C, 56.00; H, 4.00; N, 18.66. Found: C, 56.44; H, 4.41; N, 18.47.

The pyrazolone crystallizes in small rectangular plates which begin to decompose at about 200°, finally blacken completely and melt at 223°. It is soluble in methyl and ethyl alcohols and warm glacial acetic acid, and is slightly soluble in water and ether. Alkalies and acids dissolve it readily. In an alcoholic solution diluted with water it reacts acid towards litmus. With nitrous acid ($NaNO_2$ and HCl) it gives a deep red solution from which no precipitate can be obtained either by neutralizing or making alkaline. It gives brown precipitates with gold and platinum chlorides and with silver nitrate in neutral solutions a white flocculent precipitate.

Picrate, $C_7H_6N_2O_2(C_6H_2(NO_2)_3OH)$.—The picrate was obtained as a light yellow precipitate by adding an alcoholic solution of the pyrazolone to a

---

[1] *J. prakt. Chem.* [2], 39, 52.

[2] *Ibid.*, [2], **50**, 515.

[3] *Ann.*, **350**, 288.

saturated aqueous solution of picric acid. This was filtered off and crystallized from a mixture of alcohol and benzol.

Calculated for $C_{13}H_9N_5O_9$, N, 18.47. Found, 18.98.

This picrate crystallizing in small prisms with rounded ends decomposes completely at 192°, although the change begins considerably below 190°. It is soluble in alcohol, slightly soluble in hot benzene and hot water, but insoluble in ether.

Acetyl-3-furyl-5-pyrazolone, $CH_3C(:O)—C_7H_5N_2O_2$.—By warming the pyrazolone with a slight excess of acetic anhydride and pouring the solution into cold water an oil is obtained which after a while crystallizes to a mass of small radiating needles. These needles were filtered off, dried and crystallized to constant melting point.

Calculated for $C_9H_8O_3N_2$, N, 14.59. Found, 14.93.

The acetyl derivative crystallizes in long white needles melting at 153–4° to a viscous liquid. It is soluble in alcohol, hot benzene and hot ligroin but insoluble in ether and in water.

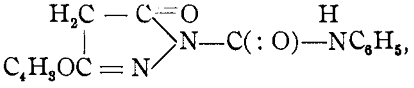
Diacetyl-3-furyl-5-pyrazolone, $C_7H_4N_2O_2(OCCH_3)_2$.—This compound was obtained by adding acetyl chloride to a pyridine solution of the pyrazolone and pouring the reaction product into cold water. The oil that separated out soon solidified and the dried product was crystallized from ligroin to a constant melting point.

Calculated for $C_{11}H_{10}N_2O_4$, N, 11.96. Found, 12.26.

The diacetate crystallizes in beautiful long white needles melting at 102° and soluble in ether, alcohol, and benzene, but insoluble in water.

Condensation Product with Phenylisocyanate, $C_7H_5N_2O_2(O:CNHC_6H_5)$.—By acting on the pyrazolone suspended in benzene with phenylisocyanate, a white compound was obtained which, after washing off the excess of phenylisocyanate, was crystallized from 90 per cent. alcohol to constant melting point.

Calculated for $C_{14}H_{11}N_3O_3$, N, 15.62. Found, 15.33.

This condensation product, which is probably furyl pyrazolone phenyl urea,  $\begin{matrix} H_2C - C{=}O & \\ | & \rangle N—C(:O)—\overset{H}{N}C_6H_5 \\ C_4H_3OC = N & \end{matrix}$, crystallizes in small white needles melting at 192° and soluble in hot chloroform, alcohol and benzene, but insoluble in water or ligroin. It may be crystallized from any one of the first three solvents.

Benzylidine-3-furyl-5-pyrazolone, $C_7H_4N_2O_2:CHC_6H_5$.—A glacial acetic acid solution of the pyrazolone was heated with an excess of benzaldehyde for about fifteen minutes on the steam bath. The mixture thickened to a brown paste which after thorough washing yielded a light brown powder. As this powder could not be crystallized, it was repeatedly washed with ether and alcohol, to remove any unconverted pyrazolone and benzaldehyde, dried and analyzed.

Calculated for $C_{14}H_{10}N_2O_2$, N, 11.75. Found, 11.47.

This compound is insoluble in most organic solvents. By heating with nitrobenzene or acetophenone, some of it dissolves, giving a red solution, but on cooling only a very small amount separates out. It does not melt at 300°. Heated with sodium hydroxide solution, it gives the odor of benzaldehyde. Concentrated sulphuric acid dissolves it, giving a red solution.

Work upon ethyl pyromucylacetate and its pyrazolone derivatives will be continued in this laboratory.

THE CONSTITUTION OF 1-PHENYL-2,3-NAPHTHALENE-DICARBOXYLIC ACID.

BY JOHN E. BUCHER.

Received June 8, 1908.

About ten years ago Michael and Bucher[1] obtained the anhydride of the above acid by the action of acetic anhydride on phenylpropiolic acid. They made a thorough study of the compound and were finally able to give conclusive proof of the correctness of the above constitution. The compound has since been obtained by a number of investigators who were evidently not aware of this work.

Lanser[2] obtained the anhydride by the action of phosphorus oxychloride on phenylpropiolic acid. He did not determine the molecular weight of the product but he described the compound as the anhydride of triphenyltrimesic acid. The formula of this compound would be $C_{54}H_{30}O_9$, corresponding to a molecular weight of 822. Michael and Bucher had shown that their compound has the composition $C_{18}H_{10}O_3$ and the molecular weight of 274.

Manthey[3] then made the compound according to Lanser's method, proving that the formula is $C_{18}H_{10}O_3$ by determining the molecular weight of its methyl ester. In addition, he showed that the anhydride is the derivative of a dibasic acid by measuring the electrical conductivity of the sodium salt. The carboxyl groups were also shown to be in the ortho position. From these facts he concluded that the acid is diphenyltetrendicarboxylic acid. These facts are not sufficient for the determination of the constitution of the compound as the following formulae show:

---

[1] *Am. Chem. J.*, **20,** 89 (1898).

[2] *Ber.*, **32,** 2478 (1899).

[3] *Ibid.*, **33,** 3083 (1900).