ethyl alcohol solution, or with dimethyl sulfate, proved unavailing, while the action of nitrous acid upon the corresponding ester of the amino acid gave chiefly the free hydroxy acid.

The free acid, used as a coupler for diazotized benzidine, gave a dark purple solution, and with diazo sulfanilic acid, in alkalin solution, a red solution.

NEW YORK CITY.

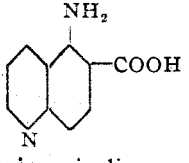
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 211.]

THE SYNTHESIS OF 1,3,7-NAPHTHOISOTRIAZINES: DERIVATIVES OF A NEW HETEROCYCLIC SYSTEM.

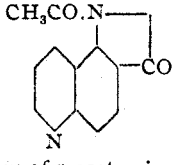
BY MARSTON TAYLOR BOGERT AND HARRY LINN FISHER.

Received September 11, 1912.

In the foregoing paper, the authors have described the preparation and properties of 5-aminoquinoline-6-carboxylic acid, its acetyl derivative, and the lactam of the latter:

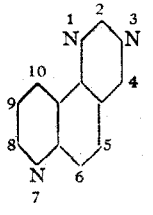


5-Aminoquinoline-6-carboxylic acid.



Lactam of 5-acetaminoquinoline-6-carboxylic acid.

From these substances, by reactions entirely analogous to those used by us in the synthesis of quinazolines,[1] we have prepared compounds containing the nucleus which, in conformity with the system of nomenclature adopted in Richter's Lexikon, we have designated the 1,3,7-naphthoisotriazine nucleus. So far as we have been able to discover, by a careful

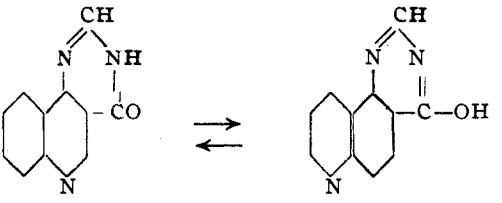


search of the literature, these are the first compounds to be described containing this nucleus, although, as all organic chemists will appreciate, it is an exceedingly difficult task to look up all possible derivatives, and we may be wrong in this assumption.

[1] THIS JOURNAL, 32, 784 (1910), and later papers in same from this laboratory.

Experimental.

4-Keto-2,3-dihydro-1,3,7-naphthoisotriazine (4-Hydroxy-1,3,7-naphthoisotriazine),[1]



One gram of 5-aminoquinoline-6-carboxylic acid was heated in a sealed tube for 6 hours at 140° with an excess of formamide. The cooled tube then contained a dark precipitate, which was boiled with sodium hydroxide solution, the solution filtered, and the filtrate saturated with carbon dioxide. The turbid solution thus obtained, on standing for two weeks, deposited dark crystals, which were purified by redissolving them in sodium hydroxide solution, filtering, diluting the filtrate, making faintly acid with acetic acid, filtering from a small amount of flocculent precipitate, and allowing the filtrate to stand for a few days. Glistening, pinkish prisms gradually crystallized out. These were separated, carefully washed with a little water, and dried at 110° to constant weight. Yield, 10%. On standing, the crystals turn light brown. They melt at 298.7° (cor.), and are soluble in methyl, ethyl, or amyl alcohol, in acetone, chloroform, benzene, or in aqueous alkalies, but are practically insoluble in ether or carbon tetrachloride.

Calculated for $C_{11}H_7ON_3$: N, 21.31. Found: N, 21.43.

Efforts to obtain the same compound, by substituting for the aminoquinoline acid its methyl ester in the above reaction, proved fruitless; but we obtained it in poor yield by heating together the amino acid and formamide in an open vessel for an hour and a half at 115–125°.

2-Methyl Derivative, $CH_3(C_{11}H_6ON_3)$.—The lactam of 5-acetaminoquinoline-6-carboxylic acid (hereinafter referred to simply as "the lactam"), when boiled with ammonium hydroxide solution, gradually dissolved to a red solution and, as the excess of ammonia was driven off, fine yellow needles separated in abundance. Recrystallized from alcohol, the compound melted with decomposition at a point above 300°, and showed marked tribo-electric properties. It is soluble in alcohol, slightly soluble in acetone or pyridine, and practically insoluble in ether, chloroform, carbon tetrachloride, benzene, carbon disulfide, petroleum ether, or ammonium hydroxide solution. In aqueous caustic alkalies it dissolves and is reprecipitated from such solutions by carbon dioxide.

For analysis, it was purified by several recrystallizations from alcohol,

[1] For the sake of uniformity, the various derivatives of this structure will be designated as ketodihydronaphthoisotriazines and formulated accordingly.

and by repeated solution in caustic alkali and reprecipitation by carbon dioxide, and then dried to constant weight at 110°.

Calculated for $C_{12}H_{11}ON_3$: C, 68.22; H, 4.30; N, 19.91.
Found: C, 68.08; H, 4.44; N, 20.26, 20.49, 20.06.

When added to a diazotized benzidine solution, it gives a brown precipitate. An attempt to form a phthalone from it by condensation with phthalic anhydride was unsuccessful.

2-Styryl Derivative, $C_6H_5.CH : CH(C_{11}H_6ON_3)$.—One gram of the compound just described was ground to a paste with a gram of benzaldehyde and 3 drops of acetic anhydride, and the mass heated for 3 hours at 180°. The melt when cold was pulverized and extracted thoroughly with boiling alcohol. This removed all contaminants and left the styryl derivative as a yellow crystallin powder, melting with decomposition above 300°. It was dried at 110° to constant weight and analyzed.

Calculated for $C_{19}H_{13}ON_3$: N, 14.05. Found: N, 14.12.

2,3-Dimethyl Derivative, $(C_9H_5N)\begin{cases} N=C.CH_3 \\ \quad\quad | \\ CO.N.CH_3 \end{cases}$.—Two grams of the lactam were treated with 20 cc. water containing slightly more than the calculated amount of methylamine, and the temperature raised to the boiling point. The lactam gradually dissolved, and on cooling, long, yellowish needles separated. Recrystallized thrice from water, the substance melted at 178° (uncor.). It is triboelectric and very easily soluble in alcohol.

Calculated for $C_{13}H_{11}ON_3$: C, 69.33; H, 4.89; N, 18.66.
Found: C, 69.65, 69.11; H, 5.45, 5.48; N, 18.74.

The *2-methyl-3-ethyl derivative* was prepared in much the same way as the foregoing, using ethylamine instead of methylamine. It forms light yellow needles, melting at 152.5° (uncor.), and is easily soluble in water or alcohol.

For analysis, it was crystallized thrice from water and dried to constant weight at 110°.

Calculated fo r $C_{14}H_{13}ON_3$: N, 17.57. Found: N, 17.80.

The *2-methyl-3-n-propyl derivative*, prepared in a similar manner, forms yellowish needles, melting at 121–122° (uncor.), readily soluble in water or alcohol.

For analysis it was crystallized twice from water and dried to constant weight at 110°.

Calculated for $C_{15}H_{15}ON_3$: N, 16.60. Found: N, 16.61.

2-Methyl-3-phenyl Derivative.—One gram of the lactam and 10 cc. aniline were boiled together for about 5 minutes, and the clear solution on cooling deposited dark crystals. These were removed, washed thoroughly with ether, and purified by crystallization from alcohol and then from acetone.

Rosets of grayish needles were thus obtained, melting at 263–263.5° (cor.); soluble in alcohol, chloroform, carbon tetrachloride or acetone, but only slightly soluble in ether.

Calculated for $C_{18}H_{13}ON_3$: N, 14.63. Found: N, 14.56.

2-Methyl-3-p-anisyl Derivative.—This was obtained similarly, by heating for $1^3/_4$ hours at 150° an intimate mixture of the lactam and *p*-anisidine in equimolecular proportion. Steam was evolved, but the mixture did not fuse at this temperature. When cold, the mass was pulverized and extracted with boiling toluene, which dissolved out the triazine. Purified by recrystallization, first from toluene and then from alcohol, it appeared in yellow, glistening plates, melting at 246.9–247.9° (cor.), soluble also in acetone or benzene, but practically insoluble in water or ether.

Calculated for $C_{19}H_{15}O_2N_3$: N, 13.24. Found: N, 13.26.

The *2-methyl-3-amino derivative* was prepared in an analogous manner, by adding 1 gram of the lactam to the calculated amount of hydrazine hydrate in 50% aqueous solution. The crude product was purified, by boiling with dilute ammonium hydroxide solution, to convert unchanged lactam to triazine, which was dissolved out by a dilute sodium hydroxide solution, the insoluble residue being then dissolved in hot dilute acetic acid and reprecipitated by ammonia. A colorless flocculent solid was obtained, melting at 256.7° (cor.), triboelectric, very slightly soluble in water, and apparently insoluble in the ordinary neutral organic solvents.

Calculated for $C_{12}H_{10}ON_4$: N, 24.78. Found: N, 24.57.

An attempt to secure a condensation of diquinazolonyl type, by using a large excess of hydrazine hydrate in proportion to the amount of lactam, resulted only in the formation of the above amino derivative.

The *2-methyl-3-acetamino derivative* was prepared from the above by the action of acetic anhydride. It crystallizes from water in colorless flocculent form, melting at 268.5–269.5° (cor.), and is soluble also in alcohol.

Calculated for $C_{14}H_{12}O_2N_4$: N, 20.89. Found: N, 21.13.

The *2-methyl-3-benzalamino derivative* was prepared by boiling the amino derivative with excess of benzaldehyde, filtering out the yellow crystals which separated on cooling, and purifying them by repeated crystallization from alcohol. The compound forms colorless fluffy branched needles, melting at 222.6° (cor.), resolidifying at 250–260°, and then darkening at about 300°.

Calculated for $C_{19}H_{14}ON_4$: N, 17.83. Found: N, 18.03.

2-Methyl-3-anilino Derivative, $(C_9H_5N)\begin{matrix}N=C.CH_3\\ |\\ CO.N.NHC_6H_5\end{matrix}$.—The interaction of pure phenylhydrazine and the lactam was so violent when the mixture was heated to the reaction point that decomposition ensued

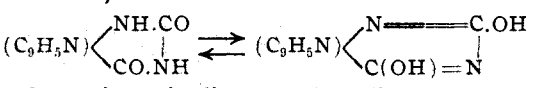
with violent ebullition. It was, therefore, necessary to dilute the phenylhydrazine with alcohol to secure a smooth reaction.

One gram of the lactam was added to a solution of 1.25 cc. phenylhydrazine in 25 cc. alcohol, and the mixture boiled gently for an hour. The lactam slowly dissolved, and a crystallin product soon separated from the solution, causing violent bumping. When the mixture had cooled sufficiently, the crystals were filtered out, washed thoroughly with cold alcohol, dried to constant weight at 110°, and analyzed.

Calculated for $C_{18}H_{14}ON_4$: N, 18.55. Found: N, 18.72.

The compound forms pale brownish needles, melting at 249.5–250.5° (cor.).

2,4-Diketo-1,2,3,4-tetrahydro-1,3,7-naphthoisotriazine(2,4-Dihydroxy-1,3,7-naphthoisotriazine).—



Equal weights of 5-aminoquinoline-6-carboxylic acid and urea were fused together. Water and ammonia were evolved during the fusion and, on cooling, a brown, hard mass was obtained. This was pulverized and extracted with cold, dilute sodium hydroxide solution, which dissolved out the dihydroxytriazine. From this solution the triazine was precipitated by carbon dioxide, or acetic acid, as a yellowish or brownish powder melting above 300°, and difficultly soluble in water or in alcohol.

Calculated for $C_{11}H_7O_2N_3$: N, 19.72. Found: N, 19.54.

With diazotized benzidine, the compound gives a dark red solution; and with diazosulfanilic acid, in alkalin solution, a deep red one.

NEW YORK CITY.

STUDIES IN THE CYCLOPENTADIENE SERIES. [I.]

2,3-DIACETYL-5-NITROCYCLOPENTADIENE.

BY WILLIAM J. HALE.

Received August 30, 1912.

The discovery of five-membered carbocyclic compounds dates from 1885, when Roscoe[1] first obtained a hydrocarbon of the formula $C_{10}H_{16}$ by the decomposition of crude phenol at a red heat. He succeeded also in separating this same hydrocarbon from the first fractions of coal tar.

The simpler form of the hydrocarbon, C_5H_6, was known to Roscoe and found to polymerize readily into the dimolecular form. It was isolated later from petroleum by Etard and Lambert[2] and called by them "pyropentylene;" the dimolecular form received the name "dipyropentylene." Nietzki and Rosemann,[3] arguing from analogy with benzene and its

[1] *J. Chem. Soc.*, **47**, 669 (1885); *Ann.*, **232**, 348 (1886).

[2] *Compt. rend.*, **112**, 945 (1891).

[3] *Ber.*, **22**, 916 (1889); see also Auerbach, *Ibid.*, **36**, 933 (1903).