Synthesis of Acetolaurolene.—Sometime ago Blanc prepared acetoisolaurolene by Friedel and Crafts' reaction and from this effected a synthesis of isocampholytic acid. It seemed possible that we might synthesize lauronolic acid by a similar process from laurolene. We have succeeded in obtaining acetolaurolene and its semicarbazone, but have not, as yet, succeeded in obtaining from this the lauronolic acid. The work will be continued and reported in detail later.

URBANA, ILL.

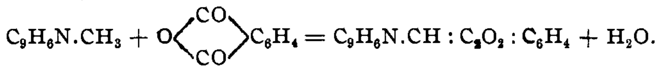
[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 201.]

RESEARCHES ON QUINAZOLINES (TWENTY-EIGHTH PAPER). ON 4-QUINAZOLONE-2-PHTHALONES AND CERTAIN OF THEIR DERIVATIVES.[1]

BY MARSTON TAYLOR BOGERT AND MICHAEL HEIDELBERGER.

Received December 25, 1911.

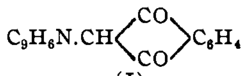
The well-known quinophthalones, or quinoline yellow dyes, are produced by condensing quinaldines with phthalic anhydride,[2] either by the action of heat alone or in the presence of such condensing agents as zinc chloride,



$$C_9H_6N.CH_3 + O\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4 = C_9H_6N.CH:C_2O_2:C_6H_4 + H_2O.$$

The product of this reaction is the alcohol-soluble quinoline yellow, or quinophthalone, which on sulfonation yields the water-soluble quinoline yellow S.

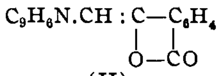
Two formulas naturally present themselves for quinophthalone,



$$C_9H_6N.CH\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_4$$

(I)

and



$$\begin{array}{l}C_9H_6N.CH:C—C_6H_4\\ \qquad\qquad\quad | \quad\ \ |\\ \qquad\qquad\quad O—CO\end{array}$$

(II)

In fact, two isomeric quinophthalones are known.

Through the skilful investigations of Eibner and his co-workers,[3] it has been proven that the one ordinarily obtained (m. 235°) possesses formula I. To the isomer (m. 186°) is therefore assigned formula II. The two compounds appear to be formed in the reaction by two distinct series of changes,[4] and neither substance is to be regarded as an inter-

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[1] Read at the Washington Meeting of the Society, December 28, 1911.

[2] Jacobsen and Reimer, D. R. P. No. 23188 (1882) and *Ber.*, 16, 513, 1082, 1892, 2602 (1883). Traub, *Ber.*, 16, 297, 878 (1883). Geigy and Königs, *Ibid.*, 18, 2407 (1885). Königs and Nef, *Ibid.*, 19, 2428 (1886). Panajotow, *Ibid.*, 28, 1511 (1895); D. R. P. Nos. 23188 and 25144. Friedländer, 1, 161, 162, *et al.*

[3] *Ann.*, 315, 303 (1901). *Ber.*, 34, 2303 (1901); 35, 1656, 2297 (1902); 36, 1860 (1903); 37, 3006, 3011, 3018, 3023, 3605 (1904); 38, 3353 (1905); 39, 2202, 2215, 2245 (1906). *Chem. Ztg.*, 28, 1206 (1904). *Chem. Zentralbl.*, 1905, I, 910.

[4] Eibner, *Ber.*, 37, 3605 (1904); *Chem. Ztg.*, 28, 1206 (1904).

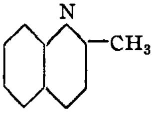
mediate product in the formation of the other. These parallel series of reactions lead, in the one case, to the formation of an alkine addition product which then passes into the unsymmetrical phthalone by loss of water; in the other case, to a quinolylacetophenone-*o*-carbonic acid which yields the symmetrical phthalone by loss of water. Both phthalones give with sodium ethylate the same red sodium salt, which with dilute acid yields the symmetrical phthalone (m. 235°). This conversion of the unsymmetrical into the symmetrical phthalone is entirely analogous to that of benzalphthalide into β-phenylindandione.[1]

In addition to the quinophthalones, phthalones have been obtained also in the pyridine,[2] benzimidazole,[3] phthalazine,[4] ethenylaminophenylmercaptan,[5] nitromethane[6] and possibly other series, but so far as we are aware none have been described as yet from the quinazoline series.

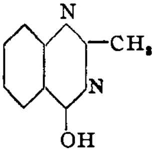
Other anhydrides, such as succinic[7] and naphthalic,[8] have been employed in lieu of phthalic, and the free acids can often be used instead of their anhydrides.

Using the imides in place of the anhydrides, analogously constituted phthalines[9] are obtained.

In the present article are described certain phthalones belonging to the quinazoline series. The 2-methyl-4-quinazolone (2-methyl-4-hydroxyquinazoline) compounds were chosen for these experiments, since they can be readily and rapidly prepared pure and in any desired amount,[10] and are of quinaldine type:



Quinaldine.



2-Methyl-4-hydroxyquinazoline.

2-Methyl-4-quinazolone condenses smoothly with phthalic anhydride to the symmetrical phthalone, which behaves as a weak acid, forming

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[1] Nathanson, *Ber.*, 26, 2576 (1893).

[2] Jacobsen and Reimer, *Ber.*, 16, 2602 (1883). von Huber, *Ibid.*, 36, 1653 (1903). Gaebelé, *Ibid.*, 36, 3913 (1903). Scholze, *Ibid.*, 38, 2806 (1905).

[3] Bamberger and Wulz, *Ber.*, 24, 2053 (1891). Bamberger and Berlé, *Ibid.*, 25, 274 (1892); *Ann.*, 273, 315 (1893).

[4] Gabriel and Eschenbach, *Ber.*, 30, 3034 (1897).

[5] P. Jacobson, *Ibid.*, 21, 2624 (1888).

[6] Gabriel, *Ibid.*, 36, 570 (1903).

[7] Eibner and Lange, *Ann.*, 315, 303 (1901).

[8] Eibner and Löbering, *Ber.*, 39, 2215 (1906).

[9] Jacobsen and Reimer, *Ibid.*, 16, 2608 (1883). Eibner and Lange, *Ann.*, 315, 328 (1901). Eibner and Hofmann, *Ber.*, 37, 3018 (1904).

[10] Anschütz, Schmidt and Greiffenberg, *Ber.*, 35, 3480 (1902). Bogert, *et al.*, THIS JOURNAL, 25, 788 (1910).

a yellow mono-sodium salt and a red di-sodium salt, as well as a red mon-anil, a mono-phenylhydrazone and a sulfonic acid. Energetic reduction converts the phthalone into the corresponding hydrindone. The sulfonic acid of the phthalone when brominated in aqueous solution yields a dibrom 2-methyl-4-quinazolone, which is not the 6,8-dibrom compound,[1] a pentabrom 2-methyl-4-quinazolone, a monobrom 2-methyl-4-quinazolone sulfonic acid, phthalic and sulfuric acids.[2] An interesting feature of the reaction is that the bromine splits off the phthalic acid from the quinazolone nucleus.

6-Nitro and 7-acetamino 2-methyl-4-quinazolone condense similarly to phthalones.

With phthalimide, 2-methyl-4-quinazolone condenses to the unsymmetrical or β-phthaline, with formation of a small amount of what appears to be a bis-quinazolone phthaline.

2-Methyl-4-quinazolone and succinic anhydride react vigorously with production of a tarry mass, from which a colorless anhydro body may be isolated.

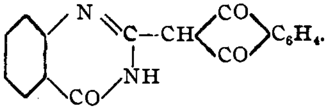
2-Methyl-4-quinazolones carrying alkyl groups in position 3 either refuse to condense with phthalic anhydride or give only a small yield of the phthalone.

In none of the experiments was the formation of any unsymmetrical phthalone observed, nor could we isolate any intermediate product except the phthalate of the quinazolone.

Like the quinophthalones, these phthalones act as yellow dyestuffs, but in tinctorial power they seem inferior to the former.

Experimental.

4 - Quinazolone - 2 - phthalone-(4 - hydroxyquinazoline - 2 - phthalone, 2 - indandionyl - 4 - quinazolone, β - (4'-quinazolonyl-2') - diketohydrindene),[3]



—An intimate mixture of equimolecular amounts of 2-methyl-4-quinazolone and phthalic anhydride was heated rapidly to about 200°. At about 160° the mixture fused to a homogeneous, yellowish brown liquid. Evolution of water began above this point, gradually becoming more rapid as the temperature rose, and finally causing the melt to boil vigorously, the color of the mixture darkening to a deep red and yellow needles separating. The mass soon solidified at this temperature (200°), but

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[1] Bogert and Hand, THIS JOURNAL, **25**, 935 (1903).

[2] Compare Limpricht, *Ann.*, **181**, 193 (1876). Kelbe, *Ibid.*, 210, 37, 48 (1881).

[3] For the sake of brevity, these compounds will be generally designated quinazolone phthalones and formulated accordingly.

the heating was continued for about three hours to complete the reaction. The crystalline brownish yellow cake thus obtained was pulverized and extracted repeatedly with small amounts of boiling 95% alcohol, to remove unchanged initial materials and certain brown by-products (see beyond). The yellow residue was then rubbed up thoroughly to a paste with sodium ethylate solution, giving at once the bright orange-red di-sodium salt. The mixture was thinned with absolute alcohol and heated for half an hour on the water-bath, to insure complete conversion to the di-sodium salt and the consequent transformation of any unsymmetrical phthalone to the symmetrical form. When cold, the mixture was filtered and the di-sodium salt rubbed up with hot water, causing immediate hydrolysis to the orange-yellow, difficultly soluble mono-sodium salt. Acidification of this with acetic acid liberated the pale yellow flocculent phthalone itself, which was filtered off, washed with hot, dilute acetic acid, then with hot water, and thoroughly dried. Average yield, 70%. As thus prepared, it was quite pure and tribo-electric. For analysis, it was again crystallized from glacial acetic acid, and then lost its tribo-electric properties:

Found: C, 70.04; H, 3.63; N, 9.88. Calculated for $C_{17}H_{10}O_3N_2$: C, 70.32; H, 3.47; N, 9.66.

Instead of the method of purification just given, the crude phthalone may be washed thoroughly with boiling dilute hydrochloric acid, then with water, and recrystallized from glacial acetic acid; or, it may be dissolved in warm, concentrated sulfuric acid, reprecipitated by dilution, and the precipitate crystallized until pure.

The pure phthalone separates from glacial acetic acid either in pale yellow prismatic needles, often united in sheaves, or in hexagonal plates. The two forms melt at the same point, and no change in melting-point occurs on mixing the two. By dissolving the plates in hot chloroform, precipitating with alcohol or ether, and recrystallizing from glacial acetic acid, the needles are obtained. It is of interest in this connection to note that pyrophthalone is also dimorphous,[1] crystallizing in both needles and leaflets, the latter being the more stable form.

Heated above 200°, the phthalone sublimes unchanged in wooly masses of pale yellow minute needles, melting at about 318° (cor.). It is very easily soluble in hot phenylhydrazine; soluble in chloroform, hot glacial acetic acid, aniline or pyridine; difficultly soluble in alcohol, acetone, amyl acetate or benzene; and practically insoluble in water or ether.

Presumably because of the—CO.NH—$\rightleftarrows$—C(OH): N—group of the quinazolone nucleus, in contradistinction to quinophthalone, it acts as a weak acid. Thus, while it is but slightly soluble in cold, dilute ammonium

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[1] Eibner and Löbering, *Ber.*, 39, 2447 (1906). Löbering, *Inaug. Dissert., Techn. Hochsch. München*, 1907, p. 47.

hydroxide solution, it dissolves readily in it on warming. In boiling sodium hydroxide or sodium carbonate solutions, it dissolves with difficulty, since the mono-sodium salt is itself difficultly soluble in alkaline solutions. From these solutions it is precipitated by acetic acid. Concentrated alcoholic potassium hydroxide solution does not decompose it, but fusion with caustic alkali or distillation with calcium oxide does. The basic properties of the quinazolone are submerged by the phthalyl residue, so that the phthalone does not form a hydrochloride or chlorplatinate under any ordinary conditions. In fact the phthalone is not only insoluble in the boiling concentrated acid, but is also very resistant to its action even when heated with it under pressure. Seven hours' heating with the concentrated acid at 190–220° left most of the phthalone unchanged; but seven hours' heating at 270° decomposed practically all of it, only phthalic acid being isolated from the blackened·tube contents. In experiments at intermediate temperatures, both phthalic acid and 2-methyl-4-quinazolone were identified among the products. In concentrated sulfuric acid, it dissolves to an orange solution, from which it separates unchanged on dilution. Hot, fuming sulfuric acid sulfonates it, while dilute nitric acid is without action upon it.

The use of zinc chloride in condensing phthalic anhydride with the quinazolone is objectionable in that it leads to the formation of tarry products and renders purification more troublesome.

Sundry experiments were carried out with the object of isolating either the unsymmetrical phthalone or intermediate products in the condensation of the quinazolone and phthalic anhydride. An intimate mixture of the two was unchanged after four hours' heating at 100°. The mixture was then dissolved in toluene and boiled gently for 72 hours, but the only change observed was a slight yellowing of the solution.

2-Methyl-4-Quinazolone Phthalate, $C_9H_8ON_2.C_6H_4(COOH)_2$.—In one experiment, ten grams of the quinazolone were mixed with an excess (14 g.) of phthalic anhydride, this excess of anhydride being added as a flux on account of the high melting-point of the quinazolone (235°) and of the phthalone, and the mixture heated an hour and a half at 150–70°, giving a yellowish brown semifluid melt. On extraction with boiling water, the crude phthalone remained undissolved (yield, about 30%), while from the aqueous extract there separated on cooling beautiful light yellow fluorescent prismatic needles of the quinazolone phthalate, carrying a molecule of water of crystallization which was driven off at 110°:

Found: H_2O, 5.50. Calculated for $C_{17}H_{14}O_5N_2.H_2O$: H_2O, 5.24.

Analysis of the anhydrous material resulted as follows:

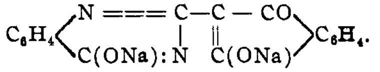
Found: C, 62.57, 62.43, 62.62; H, 4.35, 4.04, 4.38; N, 9.14, 9.03. Calculated for $C_{17}H_{14}O_5N_2$: C, 62.55; H, 4.33; N, 8.59.

Occasionally the salt crystallizes anhydrous in plates. If heated quickly to within a few degrees of its melting-point, the anhydrous salt melts at 171° (cor.) with evolution of gas. If heated above its m. p. water and phthalic anhydride are driven off and the phthalone formed, together with small amounts of decomposition products.

This phthalate is easily soluble in glacial acetic acid; soluble in alcohol, acetone, amyl acetate, nitrobenzene or hot water; difficultly soluble in chloroform; very slightly soluble in ether or hot benzene; and practically insoluble in carbon tetrachloride or ligroin. In aqueous sodium carbonate solution, it dissolves with effervescence. Its solution in aqueous potassium hydroxide solution on saturation with carbon dioxide precipitates 2-methyl-4-quinazolone. Its aqueous solution is not precipitated by silver nitrate or copper sulfate solutions. The substance is a weak dye, and in water solution dyes silk a pale greenish yellow. In concentrated sulfuric acid, it dissolves to a yellow solution which when heated to 100° and then diluted does not separate any phthalone. It seems odd that the phthalone should form a salt with phthalic and not with the strong mineral acids.

The brown alcohol-soluble by-products, formed in the condensation of the quinazolone and phthalic anhydride at 200°, were also investigated and two substances isolated: one crystalline, not melting below 313° (uncor.), the other amorphous, and melting to a tar in the neighborhood of 220–225° (uncor.). Not enough of either substance was obtained for futher study.

Di-Sodium Salt of 4-Quinazolone-2-Phthalone,



$$C_6H_4\left\langle\begin{array}{l}N{\equiv}{=}C{-}C{-}CO\\ \qquad\quad\;\; | \quad \| \\ C(ONa){:}N\;\; C(ONa)\end{array}\right\rangle C_6H_4.$$

—The phthalone was boiled for several hours with excess of an absolute alcohol solution of sodium ethylate, protecting the reflux with a calcium chloride guard tube. The orange-red salt was filtered off, dried in a desiccator, pulverized fine and washed with absolute alcohol until the washings failed to show an alkaline reaction on dilution. It was washed finally with a little absolute ether, dried *in vacuo* and analyzed:

Found: Na, 13.49, 13.50. Calculated for $C_{17}H_8O_3N_2Na_2$: Na, 13.77.

The pure salt forms an orange-red, micro-crystalline powder, which is gradually hydrolyzed by the moisture of the air to the yellow mono-sodium salt. Boiling dilute sodium hydroxide effects a similar change, but boiling water hydrolyzes it completely to the phthalone. Acetic acid immediately liberates the phthalone.

Mono-Sodium Salt, $C_{17}H_9O_3N_2Na$.—The phthalone was boiled for several hours with dilute sodium hydroxide solution, to insure complete conversion to the difficultly soluble orange-yellow salt. On filtering the hot solution, most of the salt remained on the filter, but some also separated from the filtrate on cooling. The two lots thus obtained were combined, dried at 110°, and exposed to the air, to convert any excess of caustic alkali to the carbonate (which is difficultly soluble in absolute alcohol). The crude salt was then extracted repeatedly with boiling absolute alcohol, and from these extracts the pure salt separated on cooling. It was washed with ether, pulverized, dried, and analyzed:

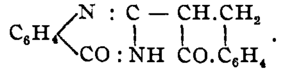
Found: Na, 7.31. Calculated for $C_{17}H_9O_3N_2Na$: Na, 7.37.

The salt as thus prepared is a pale yellowish microcrystalline solid, difficultly soluble in absolute alcohol. It is moderately soluble in water, but the aqueous solution on boiling precipitates the free phthalone. It acts as a weak dye, its aqueous solution dyeing silk a pale yellow.

Since the sodium salt of 2-methyl-4-quinazolone is colorless, while that of the quinophthalone is red, it seems most probable that the above mono-sodium salt carries the sodium in the quinazolone portion of the nucleus.

Silver Salt.—The phthalone was dissolved in dilute ammonium hydroxide solution, an ammoniacal solution of silver nitrate added, and the mixture boiled. On cooling, beautiful light yellow hair-like needles of the silver salt separated.

4-Quinazolone-2-Hydrindone,



$$C_6H_4\left\langle\begin{array}{l} N : C - CH.CH_2 \\ \quad\;\;\; | \quad\;\; | \quad\;\;\; | \\ CO : NH \;\; CO.C_6H_4 \end{array}\right. .$$

—Five grams of 4-quinazolone-2-phthalone were boiled for two hours and a half with a solution of 25 grams sodium hydroxide in 300 cc. of water, zinc dust being added in small portions from time to time. The solution slowly turned a dark green. As the solid material in the flask balled together somewhat and was protecting part of the phthalone from reduction, it was removed, rubbed up to a thin paste in a mortar, returned to the flask, the boiling with alkali and zinc dust continued for 12 hours longer, and the mixture then allowed to cool. The solid was filtered out and washed with hot water. Warming this material with dilute hydrochloric acid proved an unsatisfactory method of removing the excess of zinc, and we found it necessary to treat first with cold concentrated acid until vigorous effervescence ceased and then warm the solution until no more evolution of hydrogen occurred (several hours). The mixture was diluted with a large volume of water, boiled, allowed to cool, and the undissolved hydrindone filtered out and purified by repeated crystallization from alcohol. The yield was poor:

Found: C, 73.78; H, 4.65; N, 10.29. Calculated for $C_{17}H_{12}O_2N_2$: C, 73.88; H, 4.38; N, 10.15.

The hydrindone forms olive-yellow microscopic crystals, which sublime and turn orange above 160°, finally melting to a red liquid at about 328° (uncor.) with previous softening and decomposition. It is practically insoluble in water or ether; very slightly soluble in hot chloroform, amyl acetate or toluene; and difficultly soluble in ethyl or amyl alcohol.

In this preparation, we did not encounter any intermediate product similar to the dihydrostilbazole-*o*-carbonic acid isolated by Gaebelé[1] in his preparation of the hydrindone from pyrophthalone.

4-Quinazolone-2-Phthalone Mon-anil, $C_8H_5ON_2.\overline{CH.CO.C_6H_4.C}:N.C_6H_5$.—Eibner[2] has shown that some phthalones yield di-anils, while others give only mon-anils.

When 4-quinazolone-2-phthalone was dissolved in aniline and the solution boiled, no change occurred. But when such a solution was heated nearly to its boiling point and small amounts of anhydrous zinc chloride gradually added, an immediate and vigorous evolution of water ensued. For 5 g. of the phthalone, 3 g. zinc chloride were used. The reaction was completed by gently boiling the solution for an hour and a half, and then allowing it to cool. The pasty mass was filtered and the insoluble, bright yellow, crystalline residue washed with alcohol. Upon further addition of alcohol to the filtrate, more of the yellow solid precipitated and was added to the first lot. This yellow solid was pulverized fine, washed thoroughly with alcohol, and then with boiling, dilute ammonium hydroxide solution (to remove unchanged phthalone). From these ammoniacal extracts, on cooling, a colorless zinc salt separated. The yellow solid, as thus purified, proved to be a double zinc chloride itself, as described beyond, and gave qualitative tests for both zinc and halogen. It was decomposed by dissolving it in boiling glacial acetic acid, adding water to turbidity, then acid until clear, boiling the orange-red solution 10 or 20 minutes and cooling.[3] Minute scarlet needles separated. These were dried, extracted with boiling carbon tetrachloride, and the residue crystallized two or three times from strong acetic acid. As thus obtained, it showed only a faint trace of ash, and was analyzed with the following results:

Found: C, 75.54; H, 4.15; N, 11.99, 11.86. Calculated for $C_{23}H_{15}O_2N_3$: C, 75.59; H, 4.14; N, 11.51.

The anil crystallizes from alcohol in brilliant scarlet needles, melting at 284–5° (uncor.), with previous sublimation and sintering. It is strongly tribo-electric. In chloroform, pyridine, phenylhydrazine, or hot strong acetic acid, it is readily soluble; moderately soluble in acetone or benzene; difficultly soluble in methyl or ethyl alcohol, ether or carbon tetrachloride; practically insoluble in water or aqueous ammonium hydroxide solution. It is quite stable to mineral acids, but boiling 1 : 1 hydrochloric acid

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[1] *Loc. cit.*

[2] *Ber.*, 37, 3605 (1904). *Chem. Ztg.*, 28, 1206 (1904).

[3] Some hydrolysis of the anil often results from this boiling with strong acetic acid.

gradually hydrolyzes it to the phthalone and aniline again. Boiled for a few minutes with dilute caustic alkali solution, a light yellow alkali salt is formed, from which acetic acid liberates the red anil.

Sodium Salt.—The anil was boiled for a few minutes with excess of dilute sodium hydroxide solution. The light yellow salt was filtered off and washed thoroughly with absolute alcohol until all free alkali was removed. Some of the salt is lost by this treatment. The purified salt was dried at 110° and analyzed:

Found: Na, 5.99. Calculated for $C_{23}H_{14}O_2N_3Na$: Na, 5.94.

In presence of moisture, this yellow sodium salt rapidly hydrolyzes to the red anil. Its color is not changed by treatment with a solution of sodium ethylate in absolute alcohol.

Double Salt of Zinc Chloride and the Anil.—A portion of the crude, yellow, double zinc salt isolated as an intermediate product in the preparation of the anil was dissolved in chloroform, the solution concentrated and the salt re-precipitated by the addition of hot alcohol. The bright yellow, microcrystalline precipitate obtained on cooling was further purified by a repetition of this treatment, dried at 120–30° and analyzed:

Found: N, 9.97. Calculated for $2C_{23}H_{15}O_2N_3.ZnCl_2$: N, 9.70.

A hot alcoholic solution of the anil treated with a similar solution of zinc chloride slowly deposited on cooling a bright yellow crystalline double zinc salt apparently identical with the above.

Another Anil of the Phthalone.—In the final purification of the anil described above, the crude product was extracted with boiling carbon tetrachloride. In one case only, this orange extract, on concentration to small volume and cooling, deposited minute red crystals, melting at 258° (uncor.), with previous sublimation. Under the microscope, these crystals appeared homogeneous and on analysis gave the following figure:

Found: N, 10.91. Calculated for $(C_{17}H_9O_2N_2)_2N.C_6H_5$: N, 10.99.

This corresponds to a condensation of one molecule of aniline with two of the phthalone. The amount obtained was insufficient for further investigation, and we did not encounter it in subsequent preparations of the anil.

4 - Quinazolone - 2 - Phthalone Monophenylhydrazone, $C_8H_5ON_2.\overline{CH.CO.C_6H_4.C} : N.NHC_6H_5$.—Eibner and Hofmann[1] were unable to prepare the phenylhydrazone of quinophthalone by the direct action of phenylhydrazine upon the phthalone, but succeeded in obtaining it by the action of the hydrazine upon the anil, a reaction due to von Walther.[2]

Efforts to secure the phenylhydrazone of the quinazolone phthalone in similar fashion, from the anil, proved unsuccessful. We therefore

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[1] *Ber.*, 37, 3018 (1904).

[2] *J. prakt. Chem.*, [2] 53, 455 (1896).

heated the phthalone itself with excess of phenylhydrazine for 20 minutes over the flame. Water was given off, and the color of the solution became dark red. When cold, ether was added to the viscous mass, the orange-red precipitate filtered off, washed well with ether, and then boiled with dilute ammonium hydroxide solution to remove any unchanged phthalone. The residue crystallized twice from alcohol gave an orange-brown, microcrystalline powder, melting at about 225° (uncor.) with evolution of gas. The yield was poor and not enough of the material was obtained for further purification:

Found: N, 15.00. Calculated for $C_{23}H_{16}O_2N_4$: N, 14.74.

The compound is insoluble in water, and difficultly soluble in alcohol or amyl acetate.

An attempt to prepare the oxime of 4-quinazolone-2-phthalone by boiling the phthalone with excess of hydroxylamine hydrochloride and dilute sodium carbonate resulted merely in the immediate formation of the difficultly soluble, bright yellow mono-sodium salt of the phthalone. Eibner was likewise unsuccessful in his efforts to isolate oximes of quinophthalones.

A similar lack of success attended our efforts to prepare the semicarbazone of the phthalone. On boiling for three hours a glacial acetic acid solution of the phthalone, semicarbazide hydrochloride and fused sodium acetate, no change could be detected, even after adding a little acetic anhydride. Two grams anhydrous zinc chloride were then added and the boiling continued for four hours. On cooling the bright yellow, double zinc chloride salt of the phthalone, already described, and unchanged phthalone separated. No semicarbazone could be isolated.

4-Quinazolone-2-Phthalone-6-Sulfonic Acid, $HO_3S.C_8H_4ON_2.CH:C_2O_2:C_6H_4$.—The phthalone was dissolved in a mixture of one part concentrated to about three parts Nordhausen fuming sulfuric acid and the solution heated at 100° until a test portion dissolved completely in water (about three hours). The deep red acid solution when cold was poured upon cracked ice and most of the sulfo acid separated as a bright yellow amorphous solid. It was filtered out, and the filtrate used for the preparation of the di-sodium salt described beyond. The crude sulfo acid was boiled with a large volume of water, filtered, and the filtrate concentrated to incipient crystallization. On cooling, minute orange-yellow, glistening scales, of greasy feel, were deposited. Yield, 9 g. from 10 g. phthalone. It was recrystallized from strong (not glacial) acetic acid, dried thoroughly at 120°, and analyzed by fusion in a silver crucible with sodium hydroxide and nitrate, leaching the melt with water, and weighing as barium sulfate:

Found: S, 8.75. Calculated for $C_{17}H_{10}O_6N_2S$: S, 8.66.

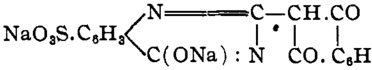
The anhydrous acid is pale yellow and dimorphous, crystallizing either in microscopic, lenticular plates or in aggregates of minute needles. The latter is the unstable form and soon changes into the plate form. On heating, the substance gradually darkens, sinters, and finally melts to a black liquid in the vicinity of 355–60° (uncor.). It absorbs moisture eagerly from the air and turns orange. It is easily soluble in hot water, but not readily in cold; very difficultly soluble in glacial acetic acid, but dissolves quite easily in the hot acid upon the addition of a small amount of water. Fusion with caustic alkali breaks it down. With concentrated nitric acid at 100°, simple nitration seems to take place, but this reaction was not followed farther. Heated for seven hours at 200° with concentrated hydrochloric acid, it is easily and cleanly split into phthalic acid and what is evidently a 2-methyl-4-quinazolone sulfonic acid. The sulfo group is therefore on the quinazolone part of the molecule, most probably at position 6.

Mono-Sodium Salt, $C_{17}H_9O_3N_2.SO_3Na$.—The free acid was dissolved in hot water, the calculated amount of sodium hydroxide added, and the solution concentrated. On cooling, the salt separated in light yellow plates, which were recrystallized from water, washed with alcohol and ether, dried to constant weight and analyzed:

Found: Na, 5.87. Calculated for $C_{17}H_9O_6N_2SNa$: Na, 5.86.

On adding sodium hydroxide to an aqueous solution of the salt, the formation of the di-sodium salt is indicated by the change in the color of the solution from a light to a dark yellow.

Di-Sodium Salt,



$$NaO_3S.C_6H_3\left\langle\begin{array}{l} N{=\!=\!=}C{-}CH.CO \\ \quad\;\; | \;\;\cdot\;\; | \qquad | \\ C(ONa):N\;\; CO.C_6H_4 \end{array}\right.\!.$$

—The filtrate from the original precipitate of crude sulfonic acid still retained considerable of this acid. It was therefore neutralized with excess of barium hydroxide solution, or barium carbonate, and the mass boiled with slight excess of sodium carbonate solution and filtered. The filtrate was concentrated, filtered from a further separation of barium salts, and evaporated to small volume. On cooling, the disodium salt separated as an orange-yellow crystalline solid, carrying water of crystallization. It was dried to constant weight and analyzed:

Found: Na, 11.01. Calculated for $C_{17}H_8O_6N_2SNa_2$: Na, 11.11.

The determination of the water of crystallization gave the following results:

Found: H_2O, 14.42, 13.98. Calculated for $C_{17}H_8O_6N_2SNa_2.4H_2O$: H_2O, 14.82.

Although this result is not very satisfactory, it appears to indicate the presence of four molecules of water of crystallization.

The presence of the sulfo group materially increases the acidity of the quinazoline portion of the molecule, and it should follow that the above di-sodium salt would carry one atom of sodium in the sulfo group and the other in the quinazoline hydroxyl, and this deduction is in agreement with the behavior of the compound. The strengthening influence of the sulfo group is evidenced also by the fact that aqueous solutions of this di-sodium salt are unchanged by boiling, whereas the corresponding mono-sodium salt of the unsulfonated phthalone is quickly hydrolyzed by such treatment.

Its aqueous solutions dye wool or silk light yellow shades. As this salt corresponds to the technical quinoline yellow S, it might be called quinazolone yellow S.

In the analysis of the sulfo acid by fusion with sodium hydroxide a brilliant red developed before the decomposition of the substance. We think that this may have been due to the formation of the tri-sodium salt, but an attempt to obtain such a red salt by the action of sodium ethylate upon the di-sodium salt was unsuccessful.

Barium Salt, $(C_{17}H_9O_3N_2.SO_3)_2Ba$.—A hot, aqueous solution of the free acid was precipitated with slightly more than the calculated amount of barium hydroxide solution, the precipitate filtered out, washed with cold water, recrystallized from boiling water, dried to constant weight and analyzed:

Found: Ba, 15.61. Calculated for $(C_{17}H_9O_6N_2S)_2Ba$: Ba, 15.46.

Minute, glistening pale yellow crystals, which are tribo-electric. It is difficultly soluble in cold water, moderately soluble in hot.

Bromination of 4-Quinazolone-2-Phthalone Sulfonic Acid.—By the action of bromine upon the aqueous solution of the sulfo acid, there were formed a di- and a penta-bromo-2-methyl-4-quinazolone, a mono-bromo-2-methyl-4-quinazolone sulfonic acid, phthalic acid and sulfuric acid.

The sulfo acid was dissolved in hot water and bromine added very cautiously until present in excess. The reaction was quite vigorous and towards its close a colorless crystalline precipitate separated which increased as the solution cooled. The mixture was allowed to stand for an hour or two and then, without removing the precipitate, boiled until the excess of bromine was driven off. A colorless solution resulted, showing that all the original phthalone sulfonic acid had been decomposed. When the mixture cooled, the precipitate was filtered out and the filtrate used for the separation of the other products of the reaction as described beyond.

Dibromo-2-Methyl-4-Quinazolone, $C_9H_6ON_2Br_2$, was isolated from the above precipitate by extraction with boiling water, and the residue used for the recovery of the pentabrom compound which follows. On cooling, there separated from these aqueous extracts arborescent masses of colorless, delicate needles. These were recrystallized from water, dried at 110° and analyzed, after a qualitative test had shown the absence of sulfur:

Found: N, 8.82; Br, 49.64. Calculated for $C_9H_6ON_2Br_2$: N, 8.81; Br, 50.28.

When heated, the compound gradually darkens and melts at about 293° (uncor.) with decomposition. It is difficultly soluble in hot water, more readily in hot alcohol or hot benzene. It is soluble also in hot, dilute potassium hydroxide solution and is reprecipitated from this solution by saturation with carbon dioxide. A comparison with the 6,8-dibromo-2-methyl-4-quinazolone of Bogert and Hand[1] shows that the two are not identical.

Pentabromo-2-Methyl-4-Quinazolone, $C_9H_3ON_2Br_5$.—After the extraction of the foregoing dibrom compound with boiling water, as described, the undissolved residue was crystallized from dilute alcohol and colorless prismatic needles of the pentabrom compound obtained:

Found: N, 5.63; Br, 72.02. Calculated for $C_9H_3ON_2Br_5$: N, 5.05; Br, 72.05.

This quinazolone melts with decomposition at about 243.5° (uncor.). It is easily soluble in glacial acetic acid or in hot alcohol; moderately soluble in chloroform, acetone, benzene or cold alcohol; difficultly soluble in ether; and practically insoluble in water. In hot, dilute potassium hydroxide solution it dissolves, and can be reprecipitated by saturating the solution with carbon dioxide.

Monobrom-2-Methyl-4-Quinazolone Monosulfonic Acid.—The filtrate from the original precipitate of crude bromquinazolones was concentrated somewhat, and to the boiling solution barium hydroxide solution was added in moderate excess and the boiling continued for 15 minutes. The heavy precipitate of barium sulfate showed that the sulfo group had been split off, at least in part, from the phthalone sulfonic acid by the bromine, and accounted for the sulfur-free quinazolones described above. The barium sulfate was filtered out and the filtrate on evaporation deposited beautiful colorless needles of the *barium salt*, contaminated with a few warty aggregates of barium phthalate which latter were readily picked out. The residual colorless needles when recrystallized from water carry from four to five molecules of water of crystallization:

Found: H_2O, 7.71. Calculated for $(C_9H_6O_4N_2BrS)_2Ba.4^1/_2H_2O$: H_2O, 7.38.

All but one molecule of this water can be driven off by drying at 110° to constant weight. The salt thus dried was analyzed by dissolving it in water, precipitating the barium with a very slight excess of sulfuric acid, and washing the precipitate thoroughly with hot water:

Found: Ba, 17.38. Calculated for $(C_9H_6O_4N_2BrS)_2Ba.H_2O$: Ba, 17.36.

This salt carrying one molecule of water is very hygroscopic.

The *free acid* was recovered from the filtrate and washings of the barium sulfate precipitate in the analysis of the barium salt. These were combined, evaporated to dryness, the amorphous residue taken up with a little hot absolute methyl alcohol, the solution reprecipitated with ether, the precipitate dissolved in absolute ethyl alcohol, filtered, the filtrate

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[1] THIS JOURNAL, 25, 935 (1903).

reprecipitated with ether, and this solution in alcohol and reprecipitation with ether repeated once more. The acid was thus obtained as a grayish amorphous solid. Like its barium salt, it retains one molecule of water of crystallization so tenaciously that it is not removed by drying to constant weight in a vacuum desiccator:

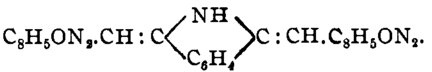
Found: N, 8.29; Br, 23.42; S, 9.79. Calculated for $C_8H_7O_4N_2BrS.H_2O$: N, 8.31; Br, 23.71; S, 9.51.

Heated in a sealed capillary, it sublimes above 200° (uncor.), partly liquefies in the vicinity of 240°, resolidifies, darkens, softens and finally melts at about 285–286.5° (uncor.). It dissolves easily in methyl or ethyl alcohol, or in water; but is practically insoluble in ether.

The filtrate from the first crystallization of the crude barium salt of this sulfo acid yielded additional amounts of barium phthalate on evaporation.

4-Quinazolone-2-Phthalines.—Eibner and his co-workers[1] found it impossible in several cases to obtain α-phthalines from their phthalones, and our experience with 4-quinazolone-2-phthalone was similar. We first heated the ammonium salt of the phthalone for 20 hours at 210° with excess of alcoholic ammonia and then, as no reaction was evident, opened the tube, added a little zinc chloride and a little more alcoholic ammonia, resealed and continued the heating for nearly 22 hours longer. There was evidence of some decomposition then, but we failed to isolate any phthaline.

Bis-(4-Quinazolone-2-)-β-Phthaline,



$C_8H_5ON_2.CH:C\Big\langle\overset{NH}{\underset{C_6H_4}{}}\Big\rangle C:CH.C_8H_5ON_2.$

—Equal amounts of phthalimide and 2-methyl-4-quinazolone were intimately mixed and the mixture heated. The mass melted to a yellowish brown liquid at about 225°, but no evolution of water occurred even at 245°. The addition of small amounts of zinc chloride, however, started the reaction immediately, and the heating was continued at 220–40° for somewhat over two hours. When cold, the dark brown mass was pulverized and extracted repeatedly with boiling, dilute acetic acid. The combined extracts on cooling deposited a reddish brown powder and, without removing this precipitate, the solution was made faintly alkaline with ammonia. The precipitate was removed, redissolved in boiling, dilute acetic acid, reprecipitated with ammonia, washed with water, dried and analyzed:

Found: N, 16.38. Calculated for $C_{26}H_{17}O_2N_5$: N, 16.25.

The amount of material available was insufficient for a complete analysis, or for a thorough study of its properties, but we believe the substance to be the bis-quinazolone phthaline.

It is an orange-brown amorphous, or micro-crystalline, solid which

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[1] *Ber.*, **37**, 3605 (1904). *Chem. Ztg.*, **28**, 1206 (1904).

when heated gradually darkens, sinters and finally forms a tar. It is soluble in alcohol, ether, dilute acetic acid, or ethyl acetate, the latter solution showing a greenish fluorescence. Its solution in dilute acetic acid acts as a powerful yellow dye, dyeing both natural and artificial silk a brilliant yellow, and unmordanted cotton thread a dull yellow.

4-Quinazolone-2-β-Phthaline, $C_8H_5ON_2.CH : \overbrace{C.CO.C_6H_4.NH}$.—The crude product of the interaction of the quinazolone, phthalimide and zinc chloride, after extraction of the bis-quinazolone phthaline with boiling dilute acetic acid, was dissolved in boiling alcohol, filtered, and the filtrate concentrated. The orange-brown micro-crystalline precipitate which separated on cooling did not appear homogeneous under the microscope and yielded appreciable amounts of quinazolone phthalone on extraction with dilute ammonium hydroxide solution. The residue was then recrystallized from alcohol and analyzed:

Found: N, 14.73. Calculated for $C_{17}H_{11}O_2N_3$: N, 14.50.

The compound crystallizes from alcohol in very voluminous aggregates of orange-brown, microscopic prisms, which sublime above 250°, sintering and decomposing at about 338° (uncor.), and finally liquefying in the neighborhood of 349° (uncor.). It is easily soluble in nitrobenzene; moderately soluble in amyl alcohol; difficultly soluble in acetone, alcohol or chloroform; and practically insoluble in water or ether. With dilute potassium hydroxide solution, it forms an orange-brown, difficultly soluble, potassium salt.

Action of Succinic Anhydride upon 2-Methyl-4-Quinazolone.—Eibner and Lange[1] failed to get the succinone of quinaldine by the direct action of succinic anhydride, since the reaction was so vigorous that only a tarry mass resulted. They finally succeeded in obtaining it, however, by heating the succinimide condensation product with hydrochloric acid, the succinone showing the characteristic yellow color of these phthalones.

In our experiment, equimolecular amounts of 2-methyl-4-quinazolone and succinic anhydride were intimately mixed and the mixture heated. At 220–30° the mixture melted to a dark brownish red liquid and began to boil from escaping steam. After heating for three hours, the melt was allowed to cool, and the black vitreous mass pulverized, boiled with dilute sodium hydroxide solution, filtered, and the dark brown filtrate acidified with acetic acid. The dark brown precipitate thus obtained was dissolved in boiling alcohol, the solution treated with bone-black, and the light yellow filtrate concentrated. On cooling, glistening gray leaflets separated, which were again treated with bone-black in alcoholic solution and crystallized to constant melting point:

Found: N, 11.73. Calculated for the succinone, $C_{13}H_{10}O_3N_2$: N, 11.57.

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[1] *Loc. cit.*

The purified substance when crystallized rapidly from alcohol separates in short, colorless microscopic prisms. On slow crystallization, some also separates in large, thin, feathery plates of pearly luster. It melts with decomposition at about 274–7° (uncor.). It dissolves in concentrated sulfuric acid to a colorless solution, and also forms a colorless salt with an absolute alcohol solution of sodium ethylate which dissolves on dilution.

In spite of the analytical result above, the absence of color from the compound and its salts renders it very doubtful as to whether it is a phthalone at all. Unfortunately, not enough of the material was isolated for a complete analysis.

6-Nitro-4-Quinazolone-2-Phthalone, $O_2N.C_8H_4ON_2.C_9H_5O_2N$.—6-Nitro-2-methyl-4-quinazolone was heated with an equal weight of phthalic anhydride for two hours at about 210°. A pasty mass was obtained which soon turned yellow. The cold melt was pulverized, thoroughly extracted with boiling water, the residue dried and then heated for half an hour with an absolute alcoholic solution of sodium ethylate. The chocolate-colored salt thus obtained was removed by filtration from the well-cooled solution. By using a sodium hydroxide solution of the proper concentration, certain dark colored impurities were extracted without dissolving much of the salt. The crude orange-red salt remaining was then washed through the filter with boiling water, and on acidifying the filtrate with acetic acid the light yellow nitro-phthalone precipitated. This was crystallized twice from nitrobenzene, washed thoroughly with alcohol, glacial acetic acid and ether, dried at 110° and analyzed:

Found: N, 12.83. Calculated for $C_{17}H_9O_5N_3$: N, 12.54.

The purified substance forms ochre-yellow, minute crystals, not melting below 355° (uncor.). It is very difficultly soluble in hot, glacial acetic acid, and practically insoluble in cold alcohol, ether, or water. The orange-red water-soluble sodium salt slowly hydrolyzes to the phthalone when its aqueous solution is boiled. The phthalone boiled with an absolute alcohol solution of sodium ethylate forms a drab salt, which changes to orange on the addition of a little water, and deposits the orange-red salt when this diluted solution is boiled. Eibner and Lange[1] found that nitro-quinophthalone lost its nitro group when boiled with dilute acids or alkalies, but we did not observe anything of this kind with the nitro-quinazolone phthalone above.

7 - Acetamino - 4 - Quinazolone - 2 - Phthalone, $CH_3CONH.C_8H_4ON_2.CH : C_2O_2 : C_6H_4$.—7-Acetamino-2-methyl-4-quinazolone[2] was heated with slightly more than an equal weight of phthalic anhydride for three hours at about 220°. Slow evolution of water began at about 190° and con-

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[1] *Loc. cit.*

[2] Bogert, Amend and Chambers, THIS JOURNAL, 32, 1301 (1910).

tinued as the temperature rose, and the mass which was pasty at first gradually hardened and became a yellowish brown. The cold melt was pulverized and thoroughly extracted with boiling water, to remove unchanged initial materials and then washed with a little cold alcohol to remove a brown impurity. The residue was heated for half an hour with an absolute alcohol solution of sodium ethylate, the mixture allowed to cool, the dark brownish red salt filtered out and ground to a paste with hot water, forming a yellowish brown, difficultly soluble salt, which was converted to the phthalone by acidifying with acetic acid. The crude phthalone was washed thoroughly with hot water, dried, and boiled ten minutes with acetic anhydride and a little fused sodium acetate, to reacetylate any liberated amine. The mixture was diluted with a large volume of water, boiled, and allowed to cool. The flocculent precipitate was filtered out, washed with hot water, recrystallized twice from glacial acetic acid, and analyzed:

Found: N, 12.28. Calculated for $C_{19}H_{13}O_4N_3$: N, 12.11.

It separates from glacial acetic acid in a voluminous mass of minute, glistening, bright yellow plates, which do not melt below 356° (uncor.). It is soluble in hot nitrobenzene or hot amyl alcohol, but insoluble in ether. Attempts to split off the acetyl group by alkali or acid resulted unsatisfactorily, the products showing a nitrogen content between that of the acetamino and that of the amino compound. This was wholly unexpected, as the 7-acetamino-2-methyl-4-quinazolone itself can be de-acetylated quite easily.

2-Methyl-3-Ethyl-4-Quinazolone, $C_2H_5.\overline{N.CO.C_6H_4.N : C}.CH_3$, was prepared by slowly adding acetanthranil to an excess of a hot (approximately 25%) aqueous solution of ethylamine containing a few drops of potassium hydroxide solution, boiling for a few minutes and then allowing the solution to cool. An oil separated which finally solidified, and was then recrystallized twice from dilute alcohol, dried to constant weight in a vacuum desiccator and analyzed:

Found: N, 15.30. Calculated for $C_{11}H_{12}ON_2$: N, 14.89.

Fine colorless needles, which melt at 67° (cor.). It is very easily soluble in alcohol, ether, acetone, chloroform or benzene; less readily soluble in hot water or petroleum ether.

Its *chlorplatinate* forms orange needles, decomposing at about 229° (uncor.):

Found: Pt, 24.75. Calculated for $(C_{11}H_{12}ON_2)_2H_2PtCl_6$: Pt, 24.83.

It is difficultly soluble in alcohol, more readily soluble in water.

Acetanthranilic Ethylamide, $C_2H_5NHCO.C_6H_4.NHCOCH_3$, was isolated as a by-product in the course of one of the experiments for the preparation of the 2-methyl-3-ethyl-4-quinazolone when no potassium hydroxide was added to the ethyl amine solution. It was easily separated from the quinazolone by fractional crystallization from dilute alcohol, in which the amide is much the less soluble. It was recrystallized twice from alcohol and analyzed:

Found: N, 13.83. Calculated for $C_{11}H_{14}O_2N_2$: N, 13.59.

It forms transparent prismatic plates, m. p. 139.5–140.5° (cor.), which are easily soluble in alcohol or chloroform; moderately soluble in ether, carbon tetrachloride, benzene or hot water.

3-Ethyl-4-Quinazolone-2-Phthalone, $C_2H_5.C_8H_4ON_2.C_9H_5O_2$.—When a mixture of about equal weights of 2-methyl-3-ethyl-4-quinazolone and phthalic anhydride was heated, a clear yellowish brown melt resulted at about 160°. Steam began to escape when the temperature was raised to 190° and the melt boiled vigorously at 200° (uncor.). Heating was continued at the latter temperature for five hours and a half. The product was a dark red, translucent viscous mass which, when left in contact with alcohol for several days at room temperature, gradually disintegrated, giving a deep red solution and depositing lemon-yellow needles. The latter were filtered off and washed with a little alcohol. An additional crop of these yellow needles was recovered by concentrating the mother-liquor. The final filtrate on dilution with water deposited a dark red oil. The yellow needles were warmed with an absolute alcohol solution of sodium ethylate for half an hour at 100°, and sufficient water then added to bring all into solution. This deep orange solution of the sodium salt was acidified with acetic acid and the light yellow phthalone precipitated. The precipitate was thoroughly washed with hot water and hot, very dilute acetic acid, and dried. Yield, 14.3%. The product was tribo-electric. On recrystallization from strong acetic acid, it lost its tribo-electric properties:

Found: N, 9.04, 9.05. Calculated for $C_{19}H_{14}O_3N_2$: N, 8.81.

From alcohol it crystallizes in beautiful bright yellow, glistening, prismatic needles, showing a faint greenish fluorescence. It melts at 198.5° (cor.), and is extremely soluble in chloroform; easily soluble in glacial acetic acid; moderately soluble in alcohol or strong acetic acid; difficultly soluble in methyl alcohol or acetone; and very difficultly soluble in ether.

By the action of heat alone, only a very slight condensation was brought about between phthalic anhydride and 2,3-dimethyl-4-quinazolone. A mixture of yellow and brown crystals was isolated from the melt, but the amount was too small to enable us to separate any pure phthalone. When the condensation was conducted in presence of zinc chloride, only a tarry mass was obtained.

2-Methyl-3-phenyl-4-quinazolone and phthalic anhydride, when condensed in presence of zinc chloride, likewise gave a tar, from which no pure phthalone could be recovered. In absence of zinc chloride, the effort to get the phthalone also proved futile.

2-Methyl-3-acetamino-4-quinazolone[1] and phthalic anhydride condensed at 220° with evolution of water, forming a violet-brown substance which dissolved in alkalies to a brown solution, and from which it was reprecipitated by acetic or dilute sulfuric acid. Not enough of the material was obtained for further investigation.

NEW YORK CITY.

THE LEAF-OIL OF THE WASHINGTON CEDAR (THUJA PLICATA).

BY ROBERT EVSTAFIEFF ROSE AND CARL LIVINGSTON.

Received December 12, 1911.

The leaf oil of the Washington cedar (*thuja plicata*) has not been examined chemically save by I. W. Brandel who published a short note on its composition.[2] The investigation referred to being only in the nature of an approximate analysis, the authors thought it advisable to undertake a more detailed study of the oil, the results of which follow: It may be mentioned that the conclusions reached differ very appreciably from those of Brandel.[3]

On steam distillation at 100°, the leaves and twigs of *thuja plicata* yield about 1% of a clear, light yellow oil which possesses the characteristic odor of cedar boughs.

The following constants were found: D_{20°, 0.913; $n_D^{20^\circ}$, 1.4552; $[\alpha]_D^{20^\circ}$, —4.77°; acid number, 0.518; ester number, 2.28; saponification number, 2.8; acetylation number, 8.8.

An elementary analysis showed the absence of sulfur and nitrogen, while the percentage composition (C = 78.6; H = 10.4) agreed very closely with that of a bicyclic ketone, $C_{10}H_{16}O$ (calc. C = 78.04; H = 10.52). The oil contained no phenols and was soluble in all proportions in anhydrous organic solvents and in 70% ethyl alcohol.

A fractional distillation under reduced pressure showed that 85% of the oil boiled between 100 and 110° under 40 mm. The small fraction (about 4%) boiling below 100°/40 mm. gave D_{20° 0.851, $n_D^{20^\circ}$ 1.4609, $[\alpha]_D^{20^\circ}$ +36.8° and was chiefly composed of pinene, which was identified by the preparation of the nitrosochloride melting at 103°. The main fraction was repeatedly distilled and yielded thus an oil boiling at 103–104° under 40 mm., which was found to be thujone by the following constants and derivatives:

$$D_{20^\circ},\ 0.9152;\ n_D^{20^\circ},\ 1.4530;\ [\alpha]_D^{20^\circ},\ —11.58^\circ.$$

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[1] Bogert and Gortner, THIS JOURNAL, 31, 946 (1909).

[2] *Pharm. Rev.*, 26, 248.

[3] *Loc. cit.*