Reference to the literature upon the separation of uranium in the electrolytic way from such metals as zinc, nickel and cobalt will disclose the fact that when using a platinum cathode with rotating anode, the uranium will be fully precipitated, but there seems to be a tendency on the part of the other metals to become enclosed in the deposit of uranium hydroxide. With this knowledge before us, it was thought worth the while to ascertain whether by employing a mercury cathode, the separations could not be made satisfactory. To this end there were made up stock solutions of zinc sulphate and uranium sulphate. Portions of these, representing 0.2071 gram of zinc and 0.1352 gram of uranium, were introduced into the mercury cup. 0.5 cc. of concentrated sulphuric acid was added, and with a current of 3.5 amperes and a pressure of 5 volts, zinc was completely precipitated in periods of time varying from 15 minutes to 60 minutes. The anode made 200 revolutions per minute. Twelve determinations were carried out with perfect success in every instance.

Cobalt and nickel sulphates were used in similar separations of these metals from uranium. The conditions were in the case of cobalt: 0.2036 gram of cobalt and 0.0322 gram of uranium, with 0.5 cc. of concentrated sulphuric acid; dilution 20 cc., current 5.6 amperes, pressure 7 volts, time 35 minutes; anode rotating 200 times per minute. The cobalt precipitated weighed 0.2034 gram. Eight determinations were made. In the case of nickel, the following conditions prevailed: 0.4290 gram of nickel and 0.0664 gram of uranium, with 0.5 cc. of concentrated sulphuric acid, and a current of 1.6 amperes, with a pressure of 5 volts. The anode performed 250 revolutions per minute. In 60 minutes there was precipitated 0.4288 gram of nickel. Eleven experiments confirmed the results of the preceding trial.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

SOME DERIVATIVES OF 2-ACETYL-NAPHTHOL-1.[1]

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

Received August 27. 1910.

The 2-acetylnaphthol-1 used in this work was prepared and converted into its 4-nitro and 4-amino derivatives according to the method of Friedländer.[2] The free base, which had an orange-red color similar to that observed by him, was treated with thioacetic acid, when the monoacetyl compound obtained melted at 212°, whereas Friedländer's acetyl de-

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[1] This research was suggested by the late Professor H. A. Torrey, and the greater part of the work was done under his direction, but the remainder of the work and the writing of the paper were deprived of the advantage of his supervision by his untimely death. C. L. JACKSON.

[2] *Ber.*, **28**, 1946 (1895).

rivative (of which he gives no analysis) melted at 107° He, however, used acetic anhydride in preparing his compound, and to make sure that our higher melting point was not due to our use of thioacetic acid we repeated the experiment with acetic anhydride and again obtained the monoacetyl compound melting at 212°. It is strange that we should have obtained a different result from Friedländer, as in at least one of our preparations we did our best to follow his directions. It is probable, however, that the difference was due to some change in conditions so trifling that we overlooked it. We regret that the pressure of other work prevented us from giving more time to this interesting subject.

Two attempts to obtain a quinoline from the 2-acetylnaphthol-1 by the method of Skraup led to unpromising results. Accordingly, we turned our attention to the method of Döbner,[1] but upon heating our amine with benzaldehyde and pyruvic acid we obtained little or no quinoline, although we tried the experiment under a number of different conditions. We are of the opinion that the process would work if tried on a large scale, but the preparation of the amine is so troublesome that such experiments did not seem worth while. The difficulty in applying Döbner's quinoline synthesis to 2-acetyl-4-aminonaphthol-1 is the more striking, because it gives essentially quantitative results with other amines. The most obvious explanation for the inertness of this amine is to be found in steric hindrance, as the acetyl group stands in the ortho position to the atom of hydrogen which should have taken part in the synthesis. It was found in the course of these experiments that the amine acts with benzaldehyde in the cold, giving 2-acetyl-4-benzylidinaminonaphthol-1, $C_6H_5CHNC_{10}H_5(OH)COCH_3$, melting at 159°. The corresponding piperonylidine compound, melting at 178°, and that containing cinnamylidine, melting at 144°, were also made without difficulty. The yields are so good that perhaps this reaction might be developed into a method for the quantitative determination of aldehydes.

In the hope of reaching a quinoline more easily, the condensation of 2-acetylnaphthol-1 with orthonitrobenzaldehyde was undertaken, for the product by reduction and elimination of water might form a quinoline but experiments with this compound and with the meta- and paranitrobenzaldehyde showed that the reaction took place with such great difficulty that it was decided to work out the method with the cheaper meta compound before attempting to prepare the desired ortho derivative. The results of the numerous experiments tried under this head were far from inviting. The metanitrobenzaldehyde reacted with the 2-acetylnaphthol-1 with great difficulty; in fact it could not be made to act at all with most catalytic agents, potassium hydroxide in alcoholic solution being the only one found effective. With this the red 2-metanitrobenzal-

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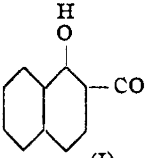
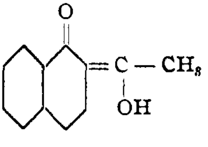
[1] *Ann.*, 249, 98, 110 (1888).

acetylnaphthol-1, $C_6H_4NO_2CHCHCOC_{10}H_6OH$, melting at 210°, was obtained, but in such small yields that it was not worth while to extend the research to the ortho compound. We can give no explanation of the fact that the nitrobenzaldehydes react with 2-acetylnaphthol-1 with so much more difficulty than the unsubstituted benzaldehyde.

During the work on the action of benzaldehydes on the 2-acetylnaphthol-1 it was noticed that this latter substance was never recovered from the experiments in the form in which it had been introduced. Instead of crystallizing in very long, pale yellowish-green needles, melting at 103°, the recovered substance crystallized in brown plates melting constantly at 98°, so that at first we thought we had a new compound. We venture to suggest that the brown form may have a quinoid structure II, while the form melting at 103° is probably the phenol, I:



(I)



(II)

This view is in harmony with the observation of v. Kostanecki,[1] that in condensing benzaldehyde and acetonaphthol with 50 per cent. sodium hydroxide it was not necessary to add an acid, as the sodium salt was decomposed merely by dilution with water. The sodium salt of a substance with a structure like II would certainly act in this way, whereas it seems impossible that the salt of a true naphthol like I could be decomposed so easily.

By condensing benzaldehyde with 2-acetyl-4-nitronaphthol-1 the 2-benzalacetyl-4-nitro-naphthol-1, $C_6H_5CHCHCOC_{10}H_5NO_2OH$, was made, which melts at 203–208°, and resembles its isomer, $C_6H_4NO_2CHCH$-$COC_{10}H_6OH$, very closely, since that melts at 210°. In fact, the only marked difference is in the color—the first being orange-yellow, the second red. It is worth noting that the nitro group attached to the benzene in the red compound is nearer the double bond than that attached to the naphthalene ring in the orange-yellow substance. 2-Benzalacetylnaphthol-1 gave with nitric acid a nitro compound, which probably contained the nitro group on the naphthalene, to judge from its orange-yellow color and the melting point 206–208°, but it is obviously impossible to decide this point with certainty, owing to the strong resemblance between the two isomers.

As the orthonitrobenzaldehyde could be obtained only with difficulty, or at considerable expense, we next searched for some more accessible orthonitroaldehyde to replace it, and such a one was found in the 6-nitro-

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[1] *Ber.*, 31, 705 (1898).

piperonal.[1] This substance had the further advantage of reacting easily even in the cold with the 2-acetylnaphthol-1, when sodium hydroxide was used as a catalyzer. The result, however, was not the condensation product expected, but the ketol, formed by direct addition of the aldehyde to the methyl of the ketone, the reaction being similar to the formation of aldol, $(CH_2O_2)NO_2C_6H_2CHO + CH_3COC_{10}H_6OH = (CH_2O_2)NO_2$-$C_6H_2CH(OH)CH_2COC_{10}H_6OH$. An intermediate addition compound like this has been frequently assumed in considering the reactions between aldehydes and the methyl of a ketone, but, so far as we can find, none has been isolated as yet in the benzene or naphthalene series, for, if we have not overlooked some of them, only two are known, one made by the action of acetaldehyde and the other by the action of chloral on acetone. This is therefore the most important observation made in this research; and it is the more remarkable that the reaction should stop at the ketol, since with the other aldehydes that have been tried the unsaturated condensation product is formed with great ease, usually even in the cold.

This ketol may be called 2-(6-nitropiperonylalcohol)acetylnaphthol-1 or 1-(naphthol-1)-1-keto-3-hydroxy-3-(6-nitro-3,4-methylenedihydroxyphenyl)-propane. Its ketol structure is confirmed by the observation that one molecule of water is removed from it by acetic anhydride, or better, zinc chloride, leaving a substance melting at 226°, which will be described presently. Our work on the acetates is also in harmony with the ketol formula, although the end of the year cut it short, before we had removed the last doubt in regard to the nature of the diacetate. Fortunately, however, the ketol formula is firmly established without the aid of this additional confirmation. Acetic anhydride alone gave with the ketol a monoacetate melting at 188–190° (in addition to the compound melting at 226°), but, if sodium acetate was also present, what is probably a diacetate melting at 197–198° was formed. The ketol melts at 201–202°, so that the melting points of these three substances lie suspiciously near together, but their properties in other respects are so unlike that there can be no doubt they are different substances. As they contain percentages of carbon, hydrogen and nitrogen, showing differences hardly greater than the experimental errors of the analysis, it is impossible to settle their composition by analysis alone. It was proved, however, that the substance melting at 188–190° is the monoacetate by the analysis of its tribromo derivative, which would leave the formula of the diacetate for the compound melting at 197–198°, if it were not for the possibility that it may be a quinoid form of the monoacetate of the ketol. This view receives some confirmation from the fact that it crystallizes in rectangular plates, thus resembling the supposed quinoid form of 2-acetylnaphthol-1 discussed earlier in this paper;

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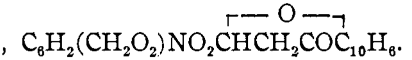
[1] Fittig and Remsen, *Ann.*, 159, 134 (1871).

but it melts higher than the other form, whereas in that case the supposed quinoid melted lower; and the analysis agrees better with a diacetate than a monoacetate formula. These facts have led us to assign the formula of the diacetate provisionally to the substance melting at 197–198°, until its composition can be definitly fixed by additional experimental work, and we are the more ready to do this, because the quinoid form in the case cited rests at present only on a theoretical basis.

The substance melting at 226°, formed by treatment of the ketol with acetic anhydride or zinc chloride, differs from it by containing one less molecule of water, which might be split out in two different ways, forming either 2-(6-nitropiperonalacetyl)-naphthol-1, $C_6H_2(CH_2O_2)NO_2CH = CHCOC_{10}H_6OH$, or (6-nitro-3,4-methylenedihydroxyphenyl)-naphthoflavanone,  $C_6H_2(CH_2O_2)NO_2\overbrace{CHCH_2COC_{10}H_6}^{O}$. The action of bromine on this substance gives a monobromo derivative formed with evolution of hydrobromic acid, and therefore pronounces in favor of the naphthoflavanone formula in spite of the fact that our substance is red, and all the flavanones, of which we can find accounts, are white, as it seems impossible that the dibromo addition product formed, if it were the piperonalacetyl compound, could be unstable enough to drop to the monobromo derivative spontaneously.

Experimental Part.

Acet-2-acetyl-4-aminonaphthol-1.—The 2-acetyl-naphthol-1 used in this work was prepared by the method of Friedländer[1] except that we found the boiling could be diminished from twenty to ten minutes, and a crystallization from glacial acetic acid removed most of the blue impurity thus facilitating the subsequent purification with alcohol. The nitro derivative also made by Friedländer's method was reduced with tin and equal parts of strong hydrochloric acid and water, added directly to the mixture of the ketone and the tin. Since the hydrochloride of the amino compound went into solution, as it was formed, it was easy to tell when the reduction was complete. The solution was filtered hot and the hydrochloride crystallizes on cooling in slightly yellowish needles, of which a small additional quantity was obtained by adding strong hydrochloric acid to the filtrate. On the addition of acid sodium carbonate to the aqueous solution of the hydrochloride the free base was obtained, of an orange-red color.

To convert this colored base into the acetyl compound, it was treated with thioacetic acid in molecular proportions, when a vigorous action at once set in, accompanied by evolution of hydrogen sulphide. The slightly yellow product, after crystallization from dilute alcohol, showed the constant melting point, 212°. As Friedländer obtained his acetyl com-

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[1] *Ber.*, 28, 1946 (1895).

pound, melting at 107°, by the action of acetic anhydride, another portion of the 2-acetyl-4-aminonaphthol-1 was warmed gently with an excess of acetic anhydride. The product was diluted, allowed to stand, neutralized with acid sodium carbonate, and the precipitate, after crystallization from alcohol, also melted at 212°.

The analysis gave 5.86 per cent. N; calculated, 5.76 per cent.

It is therefore a monoacetyl compound, as the diacetyl derivative would give N 4.91. Whether the acetyl group is attached to oxygen or nitrogen must be left undecided in the present state of our knowledge.

Properties.—It crystallizes from dilute alcohol in microscopic needles, arranged like chestnut burs, and has a yellowish white color, which we think belongs to the compound, as it could not be removed by crystallization, even when assisted by boneblack. It melts at 212° and is soluble in alcohol, chloroform, or benzene.

2-Acetyl-4-benzylidenaminonaphthol-1, $C_6H_5CHNC_{10}H_5(OH)COCH_3$.—This substance was obtained in an attempt to convert the 2-acetyl-4-aminonaphthol-1 into a quinoline. As two experiments with Skraup's method had yielded unpromising results, we tried the method of Döbner,[1] and for this purpose made a mixture of the ketone, benzaldehyde and pyruvic acid in absolute alcohol; crystals were deposited almost immediately, which, after purification, showed the constant melting point 159°. Pyruvic acid with the ketone in absolute alcohol gave no action in 30 minutes, and even after an hour only a very small amount of a green powder had been deposited from the solution, which had turned red. On the other hand, when a solution of the ketone in absolute alcohol was mixed with benzaldehyde, crystals separated almost at once. After purification these melted as before, at 159°. The yield was 95% of the theoretical.

The analysis gave 4.89 per cent. N; calculated for $C_{19}H_{15}O_4N$, 4.84 per cent.

Properties.—The benzylidene compound forms small, lustrous plates between the colors of brass and bronze. Melting point 159°. Slightly soluble in cold, soluble in hot alcohol; soluble in ether, chloroform, tetrachloride of carbon, acetone, ethyl acetate, or benzene. Ferric chloride decomposes it, forming as one of the products benzaldehyde, which was recognized by its smell.

2-Acetyl-4-piperonylidenaminonaphthol, $C_6H_3(O_2CH_2)CHNC_{10}H_5(OH)$-$COCH_3$.—This substance was obtained in almost quantitative yield by allowing solutions of the free base and piperonal in absolute alcohol to stand for fifteen minutes. It could also be obtained from the hydrochloride and piperonal, but in this case the alcoholic solution needed heat-

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[1] *Loc. cit.*

ing for thirty minutes, and the product was much less pure. After crystallization from alcohol it showed the constant melting point 178°.

Calculated for $C_{20}H_{15}O_4N$, N: 4.20. Found, 4.63 per cent.

Properties.—The piperonylidene compound forms lustrous brown plates from alcohol, which melt at 178°, and are very slightly soluble in cold, soluble in hot alcohol or tetrachloride of carbon; soluble in amyl alcohol, ethyl acetate, chloroform, or benzene; slightly soluble in gasoline. A solution of ferric chloride, if warmed slightly, turns it dark and splits off piperonal, to judge from the odor.

2-Acetyl-4-cinnamylidenaminonaphthol-1, $C_6H_5CHCHCHNC_{10}H_5(OH)$-$COCH_3$, was prepared by allowing cinnamic aldehyde to stand with the free base in absolute alcohol for thirty minutes. After crystallization from alcohol it melted constantly at 144°. The yield was 95 per cent. of the theoretical.

Calculated for $C_{21}H_{17}O_2N$: N, 4.44. Found, 4.51 per cent.

Properties.—Brownish yellow needles melting at 144°; slightly soluble in cold, soluble in hot alcohol; soluble in ether, ethyl acetate, tetrachloride of carbon, or benzene. A solution of ferric chloride set free cinnamic aldehyde, to judge by the smell.

Salicylic aldehyde gave a crystallin precipitate with an alcoholic solution of 2-acetyl-4-aminonaphthol-1, similar to those described above.

2-Benzalacetyl-4-nitronaphthol-1, $C_{10}H_5(OH)(COCHCHC_6H_5)NO_2$.—To an alcoholic solution of 10 grams of 2-acetyl-4-nitronaphthol-1 were added the equivalent amount of benzaldehyde and 20 grams of a 30 per cent. solution of sodium hydroxide and the mixture was heated on the steam bath under a return condenser for an hour. The bright red liquid thus obtained, when poured into acidified water, gave an oily precipitate, which soon crystallized. One portion of this red solid was crystallized first from glacial acetic acid and afterward from a mixture of benzene and tetrachloride of carbon; it melted between 203° and 208°. In no case did we succeed in obtaining a sharp melting point with this substance; the temperatures given are those which were not altered by subsequent crystallization. It is possible that this peculiarity of the melting point was in part due to the formation of some azoxy compound by the sodium hydroxide and alcohol, which afterward could not be removed by crystallization, and this would also explain the red color. A specimen of what we think is the same compound made by the nitric acid process (which could contain no azoxy compound) melted at 206–208°, and was orange-yellow; it therefore gives some support to this hypothesis, but it is to be observed that even this is not a sharp melting point. Another portion of the red product was recrystallized from a mixture of benzene and alcohol and melted at 202–206°. It had a reddish orange color.

Calculated for $C_{19}H_{13}O_4N$: N, 4.40. Found, 4.67 per cent.

The azoxy compound, $C_{38}H_{26}N_2O_5$, contains 4.74 per cent. of nitrogen, so that the analysis cannot distinguish between the two formulas.

Properties.—The benzalacetyl compound crystallizes from glacial acetic acid in needles of a bright orange-yellow color; but, if these yellow crystals are allowed to cool in the acid, they turn red. By heating them again with glacial acetic acid their yellow color is restored, the red form reappearing, if they are allowed to cool in the acid, whereas they remain yellow, if filtered and dried before the acid has cooled. We can offer no explanation of this phenomenon. The melting point varied according to the method of purification, 203–208° from benzene and tetrachloride of carbon, 202–206° from benzene and alcohol. Soluble in benzene; slightly soluble in alcohol, even hot, or in tetrachloride of carbon; slightly soluble in cold, much more soluble in hot glacial acetic acid.

What we suppose to be the same compound was prepared from 2-benzalacetylnaphthol-1 as follows: One gram of the ketone dissolved in hot glacial acetic acid was treated with the calculated amount of fuming nitric acid, also dissolved in glacial acetic acid. As the liquid cooled, a heavy, yellow crystallin precipitate was deposited, which, after washing with water and crystallization from a mixture of alcohol and benzene, melted at 206–208°.

Calculated for $C_{19}H_{13}O_4N$: N, 4.40. Found, 4.39 per cent.

Properties.—It crystallizes in orange-yellow needles clinging together like fibers of asbestos, which melt at 206–208°, and show the same solubilities as the substance prepared by the other method. An attempt to make a bromine derivative gave a lemon-yellow product, which could not be dried without decomposition. A specimen of the nitro compound was boiled for eight hours with tin, hydrochloric acid and alcohol without reduction, as there was no change in the melting point.

2-Metanitrobenzalacetylnaphthol-1, $C_{10}H_6OHCOCHCHC_6H_4NO_2$.—The condensation of metanitrobenzaldehyde with the ketone was a difficult affair, and we obtained little or no action with aqueous solutions of sodium hydroxide of varying strengths up to 50 per cent. tried under a variety of conditions, and we were no more successful with sodium ethylate, a saturated solution of sodium hydroxide in alcohol, zinc chloride, or barium hydroxide. Sulphuric acid of 66 per cent. gave a product, but it seemed very unmanageable. A small yield of the condensation product was finally obtained by allowing the 2-acetylnaphthol-1 and metanitrobenzalaldehyde to stand for three days at ordinary temperatures with a 20 per cent. solution of potassium hydroxide in alcohol, when a black solid was obtained, which became brownish red on drying. The filtrate from it contained unaltered acetylnaphthol. The solid was treated with water, in which it was slightly soluble, and then acidified with acetic acid, which threw down a dirty orange precipitate. This, after washing, was recrystallized from a mixture of four parts of benzene to one of alcohol, until it showed the constant melting point 210°.

Calculated for $C_{19}H_{13}O_4N$: N, 4.40. Found, 4.59 per cent.

Properties.—The metanitro compound forms red microscopic needles arranged in clusters. Melting point 210°. Soluble in chloroform; slightly soluble in hot glacial acetic acid, or hot alcohol, nearly insoluble in cold alcohol. It absorbs bromine easily, forming a vermilion-colored substance.

2(6-Nitropiperonylalcohol)acetylnaphthol-1, or 1(naphthol-1)-1-keto-3-hydroxy-3(6-nitro-3,4-methylendihydroxyphenyl)-propane, $C_{10}H_6(OH)COCH_2$-$HOCHC_6H_2NO_2(O_2CH_2)$.—This ketol was formed instead of the piperonylidene compound expected, when 5 grams of the 2-acetylnaphthol-1 and 5.3 grams of 6-nitropiperonal were dissolved in hot alcohol, cooled to the temperature of the room, and treated with 25 grams of a 30 per cent. aqueous solution of sodium hydrate. The liquid began to grow dark immediately, and soon became red, depositing a yellow solid. The action was promoted by frequent shaking, but heat must be carefully avoided, as it interfered with the success of the process. After four or five hours the dark yellow precipitate was filtered out and acidified with acetic acid. A preliminary washing with water, which was used, is not to be recommended, as the substance is soluble in water to such an extent that it was probably a sodium salt. After the acidification the substance was crystallized from glacial acetic acid till it showed the constant melting point 201–202°.

Calculated for $C_{20}H_{15}O_7N$:	C, 62.99,	H, 3.93;	N, 3.67.
Found:	C, 62.45, 62.55;	H, 2.71;	N, 4.03.

An acetate might possibly have been formed by the glacial acetic acid used in purifying the substance, and this would give very nearly the same percentages of carbon, hydrogen and nitrogen as the free ketol; therefore, to prove that our substance was not an acetate, it was boiled for an hour with strong hydrochloric acid and was recovered unaltered at the end of this time. For still greater certainty a sample was purified without the use of glacial acetic acid by crystallizing it from benzene and alcohol, when, with some difficulty, it was obtained with the same melting point and crystallin form.

Properties.—The ketol forms long, lemon-yellow needles which melt at 201–202°. It is moderately soluble in cold acetone, more so in hot; slightly soluble in ether or in cold glacial acetic acid, soluble in hot glacial acetic acid; somewhat soluble in cold, soluble in hot ethyl acetate; very slightly soluble in cold, slightly in hot alcohol; very slightly in cold, moderately in hot benzene; essentially insoluble in tetrachloride of carbon. Strong sulphuric acid dissolves it with a red color, but a yellow precipitate is formed on adding water; strong hydrochloric acid has no effect on it, even when hot; boiling with sodium hydroxide gives the 2-acetylnaphthol-1 to judge from its melting point, 98°.

A saturated alcoholic solution of the ketol turned red, when treated with piperidine, and the color became very dark after boiling for two minutes. This formed with water a red solution with a fine blue fluorescence, from which acidification threw down a yellow precipitate, but this was not studied further. The behavior of the ketol with acetic anhydride and with bromine is described later in the paper.

Monoacetate of the Ketol.—When the 2-(6-nitropiperonylalcohol)-acetylnaphthol-1 was heated in a flask with a return condenser with acetic anhydride for an hour to an hour and a half, and the product, after cooling, poured into water, two products were obtained, an orange one, which proved to be the monoacetate, and a red, which was found to be the flavanone, described later. The orange product was separated from the red by treatment with chloroform, which dissolved it, leaving the red behind. On evaporating the filtered solution the acetate was obtained nearly pure, and was recrystallized from a mixture of alcohol and benzene until it showed the constant melting point 188–190°.

Calculated for $C_{22}H_{17}O_8N$: C, 62.41; H, 4.02.
Found: C, 62.93; H, 5.10.

This analysis is of little value in determining the nature of the substance, as the free ketol contains 62.99 and the diacetate 61.93 per cent. of carbon, but that it was the monoacetate was shown by the analysis of its bromine derivative, described in the next section.

Properties.—The monoacetate crystallizes from glacial acetic acid in cream-colored needles, which melt at 188°–190°. It is soluble in chloroform; moderately soluble in cold, soluble in hot benzene; slightly soluble in cold alcohol, soluble with difficulty when hot; slightly soluble in cold, soluble in hot glacial acetic acid. Boiling with strong hydrochloric acid made it take on a brownish yellow color, but we were unable to raise the melting point of the small amount of product obtained above 188°.

Tribromo Derivative of the Monoacetate of the Ketol.—The monoacetate just described was dissolved in glacial acetic acid, the solution kept hot on the steam bath, and treated with an excess of bromine. When no more hydrobromic acid was given off the product was poured into water and the yellow precipitate thus obtained purified by repeated solution in glacial acetic acid and precipitation with water.

Calculated for $C_{22}H_{14}O_8NBr_3$: Br, 36.36. Found, 36.49 per cent.

The tribromo compound of the free ketol would contain 37.85, of the diacetate 34.98 per cent. of bromine, so there is no doubt that this compound is a monoacetate.

Properties.—The tribromo derivative crystallizes with difficulty from chloroform in small yellow needles. It has no definit melting point, but decomposes between 160 and 170°, although it turns pale green between 110 and 115°. It is moderately soluble in alcohol, or ligroin, when cold, soluble in either solvent if hot; soluble in ether, chloroform, glacial acetic acid, or benzene. After heating with sodium ethylate only a slight test for a bromide—little more than an opalescence was obtained. The bromine is therefore probably not attached to the side chain.

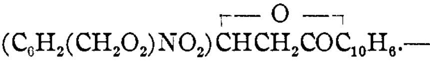
Diacetate of the Ketol.—This substance was obtained when the ketol was boiled with acetic anhydride and sodium acetate instead of with the anhydride alone. After boiling for nearly two hours, water was added which precipitated an oil, soon hardening to a pale greenish yellow solid. This was washed with water and recrystallized from benzene till it showed the constant melting point 197–198°.

Calculated for $C_{24}H_{19}O_8N$: C, 61.93; H, 4.08.
Found: C, 62.08; H, 5.64.

This analysis shows little, as the ketol and its mono- and diacetate all contain nearly the same percentage of carbon. It has been shown in the introduction to this paper that this substance is either the diacetate or a quinoid form of the monoacetate.

Properties.—The diacetate forms lustrous, golden, rectangular crystals melting at 197–198°. It is somewhat soluble in cold glacial acetic acid, or benzene, tolerably soluble in either of these solvents when hot; essentially insoluble in cold, and only slightly soluble in hot alcohol; slightly soluble in ether.

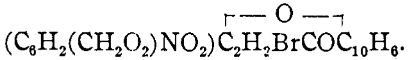
Action of Bromine on the Ketol.—This work was undertaken so near the end of the term that we have not been able to carry it beyond the preliminary stage. Bromine had no apparent action on the 2-(6-piperonylalcohol)-acetyl-naphthol-1 in the cold in chloroform suspension, but, if the ketole was dissolved in hot glacial acetic acid, and an excess of bromine added, hydrobromic acid was given off, and at the end of two or three minutes' heating on the steam bath an orange precipitate began to form, which soon became so thick that it was necessary to add more acetic acid to the pasty mass. After about three hours' heating on the steam bath, hydrobromic acid ceased to come off and the acetic acid solution was filtered from the orange-red precipitate, which formed the main product of the reaction, while a second yellow substance was obtained by the addition of water to the filtrate. That the two substances are different is shown not only by their melting point (red 252°, yellow 220°), but by their solubilities, the red compound being insoluble or nearly so in all solvents except nitrobenzene; the yellow, soluble in all the solvents tried. Two samples of the red compound gave agreeing amounts of bromine (11.83 and 11.38) on analysis, although one was purified only by washing, the other by precipitation with alcohol from a solution in nitrobenzene, but these numbers stand in no relation we can find to the monobromo ketol, which contains 17.39 per cent. of bromine. The yellow substance could not be purified sufficiently for analysis in the time at our disposal. Neither product gave up any quantity of halogen on treatment with sodium hydroxide.



2-(6-Nitro-3,4-methylenedioxyphenyl)-naphthoflavanone, $(C_6H_2(CH_2O_2)NO_2)CHCH_2COC_{10}H_6$.—This substance was made at the same time with the monoacetate by boiling the 2-(6-piperonylalcohol)-acetylnaphthol-1 with acetic anhydride. It was separated from the acetate by dissolving the latter with chloroform, in which the red flavanone was essentially insoluble. It was purified by crystallization from glacial acetic acid, until it showed the constant melting point 226°. As the yield was often very small in this process, a new method for preparing the substance was contrived, which consisted in boiling the ketol with alcohol and zinc chloride for one and a half to two hours, when the red crystals separated in good quantity.

Calculated for $C_{20}H_{13}O_6N$: C, 66.11 H, 3.59.
Found: C, 66.27, 65.95; H, 4.94, 3.39.

Properties.—The flavanone crystallizes in red needles with an orange tinge, which melt at 226°. It is essentially insoluble in ether, chloroform, or ligroin, also in alcohol, benzene, or glacial acetic acid when cold, slightly soluble in hot alcohol, very slightly in hot benzene, and soluble in hot glacial acetic acid. Bromine acts on it with the evolution of hydrobromic acid, as described in the next paragraph.



Bromine Compound of the Flavanone, $(C_6H_2(CH_2O_2)NO_2)C_2H_2BrCOC_{10}H_6$.—When the flavanone was suspended in chloroform, or dissolved in glacial acetic acid, and treated with an excess of bromine, hydrobromic acid was given off, and an orange precipitate was thrown down. To purify it for analysis it was washed thoroughly with hot glacial acetic acid, after which it showed a decomposition point between 250° and 255°.

Calculated for $C_{20}H_{12}O_6NBr$: Br, 18.09; found, 17.49, 17.49 per cent.

These analyses are as near, as could be expected, when it is remembered that the substance was purified only by washing.

Properties.—An orange powder decomposing between 250° and 255°. It is essentially insoluble in alcohol, tetrachloride of carbon, or benzene; slightly soluble in hot ethyl acetate or carbon disulphide; very slightly soluble in hot glacial acetic acid, essentially insoluble in all these solvents when cold. A drop of alcoholic potassium hydroxide added to the substance suspended in alcohol turned it red—a very bright red on warming—and gave a good test for potassium bromide. The end of the year prevented us from studying the red products of this reaction.