given. Then the assumption made that the rate of catalysis is a linear function of the concentration of undissociated acid appears to be justified, and, as was pointed out previously, the significance of this fact is that the catalysis is monomolecular with respect to the undissociated acid present in the solution.

The rate of the reaction when the concentration of hydrogen ion in the solution is very small may then be represented by the differential equation

$$-d(c)/dt = \mathrm{K}(c)$$

where c is the concentration of cinchonine salt in the solution at any time. Or, substituting for K its value given in equation (5),

$$-d(c)/dt = (\mathrm{K}' + \mathrm{A}c_1)(c)$$

This equation is evidently not a complete expression for the kinetic law of the reaction, for it does not include the retarding effect of hydrogen ion. It does, however, indicate that the reaction of the conversion of cinchonine to cinchotoxine is made up of at least two reactions going on simultaneously; one of these reactions proceeding without the aid of a weak acid, and the other involving the weak acid. It is hoped that future work will make it possible to determin this law completely.

Summary.

1. The specific reaction rate for the change of cinchonine to cinchotoxine by the catalytic action of acetic acid in large excess has been determined for two concentrations of acetic acid.
2. The reaction has been found to be monomolecular with respect to the alkaloid, and the catalysis has been found to be monomolecular with respect to undissociated acetic acid.
3. It has been found that acetate ion has little or no effect on the speed of the reaction.
4. At low concentrations of hydrogen ion the retarding effect of this substance has been found to be very small.

BERKELEY, CAL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

HYDRAZONES OF OXY-ALDEHYDES AND KETONES; ALKALI-INSOLUBLE NAPHTHOLS.[1]

BY H. A. TORREY AND C. M. BREWSTER.

Received January 21, 1913.

In an earlier paper of the series on phenols insoluble in alkalies, H. B. Kipper and one of us[2] pointed out that in the compounds they had studied

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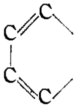
[1] This research was suggested by the late Professor H. A. Torrey, and the experimental work was done under his direction, but the writing of the paper was deprived of the benefit of his supervision by his too early death.—C. L. JACKSON.

[2] THIS JOURNAL, **30**, 841 (1908); see also *Ibid.*, **29**, 77 (1907).

the insolubility in aqueous alkalies was determined by the two following conditions: (1) the free hydroxyl group is ortho to a large side chain, (2) other substituting groups are present on the benzene ring to which the hydroxyl is attached. The substituting groups which have been proved effective in producing insolubility are methyl, methoxyl, ethoxyl, acetoxyl, benzoxyl, $CH_3\overset{|}{C} = NNHC_6H_5$ and $C_6H_5\overset{|}{C} = NNHC_6H_5$.

In taking up the subject we have studied both sets of conditions and especially another effective group not mentioned under (2). This is the



group of naphthalene to which attention has also been called by Goldschmidt and Brubacher.[1] Our later work has brought to light eighteen naphthol derivatives which are insoluble in alkalies. In fact this group seems to be more effective in producing insolubility than any other as yet studied, since the azine of 2-acetonaphthol is insoluble in alkalies, whereas the azines of all other phenol derivatives so far tried are soluble. Our work has not indicated any marked difference between derivatives of acetonaphthol and naphthaldehyde; the phenylhydrazones, *p*-bromophenylhydrazones, benzylphenylhydrazones, α- or β-naphthylhydrazones, and benzidine compounds of the two show the same insolubility in aqueous alkalies. The azine of β-naphthol-α-aldehyde may be an exception to this statement, as it is soluble, while the azine of β-aceto-α-naphthol is insoluble, but it seems to us much more probable that the difference in this case is due to the difference in position of the hydroxyl and side-chain (β-α in the aldehyde and α-β in the ketone). It is hoped that this suggestion can be tested by experiment in the near future.

Bromine when attached to the benzene ring of the phenol seems to have no appreciable effect on its solubility in alkalies, for the 5-bromosalicylaldehyde phenylhydrazone and the 3,5-dibromosalicylaldehyde compound are dissolved by aqueous sodium hydroxide, and it was found that the introduction of bromine into the naphthol nucleus did not appreciably affect the solubility of the compound; but on the other hand the parabromophenylhydrazone of salicylaldehyde was less soluble in alkalies than the phenylhydrazone, so that bromine seems to have a feeble tendency to reduce the solubility, which, however, is not strong enough to appear in the compounds mentioned at first.

The introduction of a nitro group para to the phenol hydroxyl increased the solubility in alkalies, as the phenylhydrazone, parabromophenylhydrazone, and α- or β-naphthylhydrazone of 2-aceto-4-nitro-1-naphthol were all soluble, while the corresponding substances without the nitro group were not; but this observation probably has no bearing on the solu-

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[1] *Ber.*, 24, 2306.

bility of phenols, as the effect may be due to the formation of salts of a quinolnitro acid,[1] in which case the phenol hydroxyl takes no part in it.

The effect of varying the ortho side chain (1) upon the solubility of phenols in alkalies was also studied; in the first place, starting from 2-aceto-1-naphthol, its size was increased by the condensation of aldehyde with the methyl, which showed that the derivatives from benzaldehyde, para-nitrobenzaldehyde, piperonal, or furfural, dissolved in 10% but not in 30% solutions of sodium hydroxide, even when the latter were warm, so that these substances must be assigned to an intermediate class of phenols soluble with difficulty in alkalies. These phenomena seem to point to the formation of a sodium salt insoluble in strong solutions of sodium hydroxide, but this explanation is excluded by the following experiment: Two grams of benzalbromoacetonaphthol were placed in a test tube with 20 cc. of 30% sodium hydroxide solution, and allowed to stand for three days, when the liquid was decanted off, and on neutralization with hydrochloric acid no precipitate was formed, showing that none of the original compound had dissolved in the alkali. The residue was treated with a large excess of water (200 cc.), in which it did not dissolve, and after this water had been in contact with the residue for more than a week, it was acidified but showed no trace of a precipitate. In view of this, it seems hard to escape the conclusion that steric hindrance is one of the causes of the insolubility of the phenols in alkalies. It may be also that the complete insolubility of the phenylhydrazones is in part due to the closer proximity of these large groups to the phenol hydroxyl, since they stand on the first instead of the second carbon atom of the side chain, but the positive nature of the hydrazone undoubtedly also has an influence on the solubility. We have mentioned this case principally to show that the effect is probably due to a combination of several causes, and also that it is not wise to attempt to reach definit conclusions with the facts at present at our disposal.

To the group completely insoluble in aqueous alkalies belong the phenylhydrazone of 2-aceto-1-naphthol, the parabrom- or metanitro-phenylhydrazone, the benzylphenylhydrazone, and the α- or β-naphthylhydrazone; also its condensation products with β-naphthylamine, benzidine, and hydrazine. It was obvious that in these compounds the effect of the naphthalene group in the acetonaphthol reduced the solubility so much that no comparative results were possible; accordingly, experiments were repeated with salicylaldehyde, the phenylhydrazone of which is soluble in cold aqueous alkalies. It then appeared that the parabromophenylhydrazone of salicylaldehyde is only slowly soluble in boiling 10% sodium hydroxide, while the benzylphenylhydrazone, $C_6H_4OH.CH.NNC_7H_7C_6H_5$, is insoluble in cold and soluble only with difficulty in boil-

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[1] *Am. Chem. J.*, 24, 99 (1903).

ing sodium hydroxide solutions; so that substitutions in the hydrazone in these cases at least diminish the solubility.

Some other compounds with side chains which gave soluble derivatives of the acetonaphthol were prepared; these were the oxime, the paraminophenol derivative, and the semicarbazone, but these do not come into the discussion of the question, as each of them contains an acid hydrogen which would render the substance soluble in sodium hydroxide, even if the naphthol hydroxyl took no part in the action.

Experimental Part.

The following compounds discovered in the course of this work have been described already elsewhere:[1] Monobromo-α-acetonaphthol, benzylidine bromo-α-acetonaphthol, acetonaphthol phenylhydrazone, bromoacetonaphthol phenylhydrazone, acetonaphthol *p*-bromophenylhydrazone, bromoacetonaphthol *p*-bromophenylhydrazone, acetonaphthol *m*-nitrophenylhydrazone, bromoacetonaphthol *m*-nitrophenylhydrazone, all of which, with the exception of the first two, are insoluble in alkalies.

Derivatives of 2-Acetonaphthol-1.—The acetonaphthol used in this work was prepared by the method of Friedländer[2] with a slight modification already described.[3] Under certain conditions a modified form of this compound was obtained, apparently an isomer. If a small quantity of aniline or salicylaldehyde was added to a strongly alkaline alcoholic solution of acetonaphthol and the mixture refluxed for several hours, the clear solution on dilution or careful neutralization gave a product which crystallized from benzene and ligroin in bright yellow, lustrous plates very different in appearance from the pale yellow-green needles of the original acetonaphthol. Its melting point was slightly different (98° instead of 103°), and it was more readily soluble in alcohol and other solvents. When recrystallized repeatedly from alcohol the body gradually changes back to the original form, melting at 103°.

The phenylhydrazone of 2-acetonaphthol-1 has been described already.[3] In the hope of determining whether it had a phenol or quinoid structure, it was treated with hydroxylamine as follows: The phenylhydrazone was dissolved in alcohol and mixed with the hydrochloride of hydroxylamine dissolved in a little water, and an aqueous solution of potassium hydroxide in the proportion of three molecules of the hydrochloride and nine of the potassium hydroxide to each molecule of the hydrazone. The mixture was heated under a return condenser for four hours, the clear yellow solution poured into water and carefully neutralized with dilute hydrochloric acid when a flocculent, pale yellow precipitate was thrown down, which was crystallized from alcohol until it showed the

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[1] Torrey and Brewster, THIS JOURNAL, 31, 1322 (1909).

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

[3] THIS JOURNAL, 31, 1322 (1909).

constant melting point 167°–169°. On a comparison of its physical and chemical properties with those of a sample of the oxime of 2-aceto-naphthol-1 prepared according to Witt,[1] they were found to be identical, so the hydroxylamine radical has replaced the phenylhydrazine radical.

2-Aceto-naphthol-1-α-naphthylhydrazone, $C_{10}H_6OHC(NNHC_{10}H_7)CH_3$.—All these hydrazones were prepared by heating the acetonaphthol with the hydrazine on the steam bath, a little more than one molecule of the hydrazine being used for each molecule of the naphthol. In this case the heating was carried on for half an hour.

Calculated for $C_{22}H_{18}N_2O$: N, 8.61; found, 8.92.

Nearly white crystallin substance melting at 179°–180°. Soluble in alcohol, chloroform, carbon tetrachloride, benzene, ligroin, or glacial acetic acid; almost insoluble in ether. Strong sulfuric acid gives a deep olive-green solution depositing a bright yellow precipitate on dilution; ferric chloride with a cold dilute solution gives a dark yellow color changing to blood red on standing; *insoluble in a boiling solution of sodium hydroxide.*

2-Aceto-naphthol-1-β-naphthylhydrazone.—After boiling two hours the product was precipitated with water and recrystallized from alcohol until it melted constantly at 174°–176°.

Calculated for $C_{22}H_{18}N_2O$: N, 8.61; found, 8.75.

This reaction took place with much greater difficulty than that of the α compound, and the yield was relatively small. Yellowish brown crystals melting at 174°–176°. Soluble in alcohol, benzene, ligroin, or glacial acetic acid. Strong sulfuric acid formed a deep orange-red solution; the substance is *insoluble in warm 10% aqueous solution of sodium hydroxide.*

2-Aceto-naphthol-1-benzylphenylhydrazone, $C_{10}H_6OH.(NNC_7H_7C_6H_5)CH_3$.—The materials were boiled one and a half hours. Longer boiling did not increase the yield, which amounted to about 70% of the theoretical. The hot, brilliant yellow solution thus obtained was diluted to the point of precipitation when upon cooling it deposited yellow needles, which were warmed with successive portions of a dilute solution of sodium hydroxide until the liquid gave no turbidity on acidification. After it had been freed in this way from unaltered acetonaphthol it was recrystallized from alcohol until it showed the constant melting point of 130°–132°.

Calculated for $C_{25}H_{22}N_2O$: N, 7.65; found, 7.88.

Fine yellow needles melting at 130°–132°. Ferric chloride imparts a slightly deeper yellow color to the alcoholic solution. It is *entirely insoluble in a boiling 10% solution of sodium hydroxide in water.*

2-Aceto-naphthol-1-azine, $(C_{10}H_6OH.CCH_3)_2N_2$.—An aqueous solution of hydrazine sulfate was added to an alcoholic solution of the acetonaph-

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[1] *Ber.*, 21, 323 (1888).

thol in the proportion of one molecule of the former to two of the latter, and solid sodium hydroxide was also added in the proportion of two molecules. After boiling the mixture for thirty minutes a heavy flocculent precipitate of the azine had formed and the mixture was diluted with four times its volume of alcohol, cooled rapidly, and filtered. The orange precipitate was washed with alcohol and crystallized from freshly distilled boiling aniline.

Calculated for $C_{24}H_{20}N_2O_2$: N, 7.60; found, 7.44.

Brilliant light orange crystals which decompose at a high temperature. It is insoluble in the usual organic solvents but dissolves in boiling aniline. Strong sulfuric acid forms a bright red solution with it, which becomes colorless when warmed. It was not decomposed by continued boiling with dilute acids even in the presence of alcohol. It is *entirely insoluble in a 10% warm solution of sodium hydroxide in water.* It was boiled with a 30% aqueous sodium hydroxide solution for three hours without dissolving or giving a perceptible color to the solution, and when allowed to stand with concentrated sodium hydroxide solution for six months, it remained unchanged.

2-Aceto-naphthol-1-azine Monoacetate.—This was made by boiling 1.5 grams of the substance just described with 15 grams of acetic anhydride and 3 grams of fused sodium acetate until the azine was completely dissolved. For the first ten to twenty minutes there was no perceptible change, then the compound suddenly turned deep red and in less than a minute resumed its pale orange color; after this the solution took place rapidly and was complete after boiling from forty minutes to an hour in all. Water was added to the cooled mixture and the excess of acetic anhydride removed with acid sodium carbonate, when a yellow amorphous powder was obtained, which was filtered out, washed, and dried in a desiccator. It was then dissolved in benzene, filtered, the filtrate evaporated to dryness, and the residue dissolved in a small quantity of benzene. Three volumes of hot ligroin were added and on standing grayish white crystals were deposited, which were recrystallized from the same mixture until they showed the constant melting point 169°–170°.

Calculated for $C_{26}H_{22}N_2O_3$: N, 6.83; found, 7.21.

2-Aceto-naphthol-1-benzidine, $(C_{10}H_6OH.CCH_3)_2N_2(C_6H_4)_2$. — The aceto-naphthol, benzidine, and fused zinc chloride were ground together to a fine powder and the mixture heated in an oil bath at 150° until the effervescence ceased, which usually required ten to twenty minutes. The fused product was extracted with boiling water and afterwards with successive portions of alcohol.

Calculated for $C_{36}H_{28}N_2O_2$: N, 5.40; found, 5.80.

A light red amorphous powder which decomposes at 210°. It is insoluble in all the usual organic solvents, but when boiled with aniline, nitrobenzene, or glacial acetic acid, a bright yellow substance is formed, evidently a new product because it dissolves in sodium hydroxide. The red benzidine compound is decomposed by boiling several hours with dilute acids and is *insoluble in a boiling aqueous solution containing 10 or 30% of sodium hydroxide.*

2-Aceto-naphthol-1-semicarbazone, $C_{10}H_6OH.C(NNHCONH_2)CH_3$.—An alcoholic solution of acetonaphthol, and semicarbazine hydrochloride, in molecular proportions, and a slight excess of sodium hydroxide was boiled for an hour, when a few drops of hydrochloric acid threw down a heavy yellow precipitate from a hot solution. This was filtered out and redissolved in a dilute solution of sodium hydroxide, filtered, and precipitated again with hydrochloric acid. It was purified by washing with hot alcohol.

Calculated for $C_{13}H_{13}N_3O_2$: N, 17.15; found, 17.28.

A pale yellow powder melting at 245°–250°. Soluble with difficulty in alcohol, benzene, or acetic acid. Ferric chloride produces a deep green color in the aqueous solution. *It dissolves easily in cold aqueous sodium hydroxide.*

2-Aceto-naphthol-1-β-naphthylamine, $C_{10}H_6OHC(NC_{10}H_7)CH_3$. — Equal weights of powdered acetonaphthol and β-naphthylamine mixed with fused zinc chloride were heated in an oil bath to 200° for fifteen minutes and the product, after extraction with dilute hydrochloric acid and boiling with alcohol, was dissolved in acetone, filtered and precipitated with water.

Calculated for $C_{22}H_{17}NO$: N, 4.50; found, I, 4.79, II, 4.42.

A bright yellow, amorphous powder, melting at 161°–162°. It gives no color reaction with ferric chloride, and is *insoluble in a boiling aqueous 10% solution of sodium hydroxide.*

2-Aceto-naphthol-1-paraminophenol, $C_{10}H_6OHC(NC_6H_4OH)CH_3$. — Prepared by heating equal quantities of the two components with fused zinc chloride to 180°–200° for three hours. The black product, after boiling with water till free from zinc salts, was extracted with warm 80% alcohol as long as the extract was strongly colored. This left a mass of dark green scales which were crystallized twice from glacial acetic acid and after washing with alcohol dried for analysis.

Calculated for $C_{18}H_{15}N_2O_2$: N, 5.05; found, 5.03.

Dark green lustrous scales which decompose between 210°–220°. Soluble with difficulty even in hot alcohol; soluble in glacial acetic acid. *Easily soluble in cold aqueous sodium hydroxide.*

1,5-Diphenyl 3-α-Naphthol Pyrazoline, $C_{10}H_6OH.C_3H_3N_2.(C_6H_5)_2$.—Benzalacetonaphthol was prepared according to the method described by St. v. Kostanecki,[1] and was treated with phenylhydrazine in the hope of ob-

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[1] *Ber.*, 31, 708 (1898).

taining the hydrazone. The above substances in molecular proportion were dissolved in glacial acetic acid and the solution boiled for 24 hours. The reaction mixture was filtered hot and allowed to stand for a day, after which the compound was precipitated out by adding small quantities of water at intervals of an hour or more, until no more of the substance separated from solution. Too rapid dilution gives a milky liquid from which it is very difficult to obtain a crystallin product. The compound was further purified by crystallization from hot glacial acetic acid, or by dissolving in benzene and gradually adding alcohol to the solution.

Calculated for $C_{25}H_{20}N_2O$: N, 7.69; found, 7.76.

The light yellow, granular product melts with decomposition at 189°. It dissolves in benzene, ligroin, and hot glacial acetic acid, but is difficultly soluble in alcohol. A dilute alcoholic solution gives a light yellow color on addition of ferric chloride; on standing the color deepens to a dark brown. An attempt to reduce the compound by means of sodium amalgam with the production of aniline was unsuccessful, and the substance could not be hydrolyzed by boiling for several hours with dilute hydrochloric acid and alcohol. *It is insoluble in boiling 10% or 30% aqueous sodium hydroxide solution.*

When a minute particle of the substance is dissolved in concentrated sulfuric acid and a drop of ferric chloride or of sodium nitrite solution added, the characteristic blue color test of pyrazolines is produced.[1] As shown by the work of Auwers,[2] the continued boiling with acetic acid tends to bring about the formation of a five-membered ring in compounds of this nature.

Monobromo-2-aceto-naphthol-1-acetate, $C_{10}H_5BrOC_2H_3O.COCH_3$.—To 5 grams of the bromoacetonaphthol described in our previous paper[3] were added 18 grams of acetic anhydride and 5 grams of fused sodium acetate, and the mixture was boiled under a reverse condenser until a drop of it dissolved in alcohol gave no green color with ferric chloride, which usually required an hour and a half. Too long boiling produced a tarry decomposition product. After the excess of acetic anhydride had been removed with acid sodium carbonate, the brown residue was dissolved in hot alcohol, boiled with bone-black, filtered, and the filtrate diluted with 30% of water, when a crystallin mass was deposited which was recrystallized from alcohol.

Calculated for $C_{14}H_{11}BrO_3$: Br, 26.06; found, 26.36.

Nearly colorless crystals which melt at 95°–96°. It is soluble in alcohol, ether, or benzene; *insoluble in cold sodium hydroxide solution* but gradually decomposes when warmed.

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[1] Knorr, *Ber.*, 26, 101 (1893).

[2] K. Auwers and H. Voss, *Ber.*, **42**, 4411 (1909).

[3] THIS JOURNAL, **31**, 1322 (1909).

Monobromo-2-aceto-naphthol-1-α-naphthylhydrazone, $C_{10}H_5BrOHC(NNHC_{10}H_7)CH_3$.—This substance was made in the same way as the unsubstituted compound and purified by crystallization from alcohol.

Calculated for $C_{22}H_{17}BrN_2O$: N, 6.91; found, 6.72.

Light brown crystals which melt with decomposition at 175°–176° *Insoluble in a boiling 10% aqueous solution of sodium hydroxide.*

Monobromo-2-aceto-naphthol-1-β-naphthylhydrazone, $C_{10}H_5BrOHC(NNHC_{10}H_7)CH_3$.—Purified by crystallization from alcohol.

Calculated for $C_{22}H_{17}BrN_2O$: N, 6.91; found, 6.40.

Slightly pink granular crystals which melt with decomposition at 184°–186°. Soluble in alcohol, benzene, or glacial acetic acid. *Insoluble in a warm aqueous 10% solution of sodium hydroxide.*

Monobromo-2-aceto-naphthol-1-benzylphenylhydrazone, $C_{10}H_5BrOHC(NNC_7H_7C_6H_5)CH_3$.—Prepared and purified like the unsubstituted compound.

Calculated for $C_{25}H_{21}BrN_2O$: Br, 17.97; found, 18.13.

Light yellow crystals melting at 125°–126°. Ferric chloride imparts a slightly deeper yellow color to the alcoholic solution. *Insoluble in a warm aqueous 10% solution of sodium hydroxide.*

Monobromo-2-aceto-naphthol-1-oxime, $C_{10}H_5BrOHC(NOH)CH_3$.—An excess of an aqueous solution of the hydrochloride of hydroxylamine was added to an alkaline solution of bromoacetonaphthol and the mixture allowed to stand for half an hour, after which it was filtered and the filtrate carefully neutralized with hydrochloric acid; the heavy white precipitate was purified by crystallization from alcohol, or from benzene and ligroin.

Calculated for $C_{12}H_{10}BrNO_2$: N, 4.83, found, 4.96.

Pale yellow crystals which melt with decomposition at 189°–190° and are turned deep brown by exposure to direct sunlight.

Ferric chloride gives an intense green with its cold alcoholic solution. *With sodium hydroxide a green salt is formed which is soluble with difficulty.*

Monobromo-2-aceto-naphthol-1-semicarbazone, $C_{10}H_5BrOHC(NNHCONH_2)CH_3$.—Prepared and purified like the unsubstituted compound.

Calculated for $C_{13}H_{12}BrN_3O_2$: N, 13.04; found, 12.50.

A pale yellow, amorphous powder, which has no melting point but decomposes at a high temperature. It is soluble with difficulty in the usual organic solvents. Strong sulfuric acid gives an orange solution; dilute hydrochloric acid does not decompose it, even when boiled for an hour with it, but if alcohol is present it is converted into bromoacetonaphthol. Ferric chloride gives a dark green color. *It is easily dissolved in dilute aqueous alkalies.*

Monobromo-2-aceto-naphthol-1-azine, $(C_{10}H_5BrOHCCH_3)_2N_2$.—This was made and purified like the unsubstituted compound.

Calculated for $C_{24}H_{18}Br_2N_2O_2$: N, 5.32, Br, 30.30; found: N, 5.46, Br, 30.09.

It crystallizes from freshly distilled aniline in fine, bright orange needles, which decompose at a high temperature. Difficultly soluble in chloroform or carbon tetrachloride; insoluble in alcohol, ether, acetone, benzene, or ligroin; soluble in hot aniline. Strong sulfuric acid forms a scarlet solution which becomes colorless on warming. *Insoluble in a boiling aqueous 10% solution of sodium hydroxide.*

4-Nitro-2-aceto-naphthol-1-phenylhydrazone, $C_{10}H_5NO_2OHC(NNHC_6H_5)CH_3$.—The 4-nitro-2-acetonaphthol-1 was made by the method of Friedlander,[1] but a sufficiently good product was obtained more cheaply as follows: Freshly pulverized acetonaphthol was mixed with nitric acid of 30–50% and the mixture allowed to stand for 10–15 hours, precipitated with water, and washed free from acid.

The hydrazone was also prepared by Friedländer[1] but he gives no analysis. Nitroacetonaphthol dissolved in hot glacial acetic acid was added to an acetic acid solution of phenylhydrazine in molecular proportions and the mixture boiled one hour. The crystals which separated on cooling were recrystallized from glacial acetic acid.

Calculated for $C_{18}H_{15}N_3O_3$: N, 13.08; found, 13.32.

Red needles which sinter at 221° and melt with decomposition at 222°–223°. It is decomposed by dilute hydrochloric acid and alcohol if the mixture is boiled four hours but not by the acid alone under the same conditions. Ferric chloride has no immediate effect on an alcoholic solution but on standing a deep reddish brown color appears. It imparts a red color to a cold *10% aqueous solution of sodium hydroxide* and *gradually dissolves when the solution is heated.* It is precipitated unchanged from this solution by acids. *It is insoluble in a 30% solution of sodium hydroxide and is decomposed if boiled with it, forming an oily film on the surface of the liquid.*

4-Nitro-2-aceto-naphthol-1-phenylacethydrazoneacetate, $C_{10}H_5NO_2OOCCH_3C(NNOCCH_3C_6H_5)CH_3$.—To 2 grams of the hydrazone described above were added 18 grams of acetic anhydride and 3 grams of fused sodium acetate, and the mixture was boiled for one hour. The excess of acetic anhydride was removed with acid sodium carbonate solution and the brown residue washed and dried at room temperature. The dry product was extracted with warm benzene, and the residue dissolved in alcohol, boiled with bone-black, filtered, and the filtrate diluted with 20% of hot water and allowed to stand until cool, when fine crystals separated from solution.

Calculated for $C_{22}H_{19}N_3O_5$: N, 10.37; found, 10.66.

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[1] *Ber.*, 28, 1949 (1895).

Fine white crystals, which sinter at 196° and melt without decomposition at 197°–198°. It is easily soluble in acetone, difficultly soluble in benzene and alcohol, and insoluble in ligroin and carbon tetrachloride.

4-Nitro-2-aceto-naphthol-1-parabromophenylhydrazone, $C_{10}H_5NO_2OHC(NNHC_6H_4Br)CH_3$.—Prepared and purified like the unsubstituted compound.

Calculated for $C_{18}H_{14}N_3BrO_3$:	N, 10.50;	Br, 20.00.
Found:	N, 10.59, 10.39;	Br, 19.96.

Dark red, needle-like crystals, which melt with decomposition at 257°–258°. It is difficultly soluble in alcohol, acetone, carbon tetrachloride, and glacial acetic acid. With concentrated sulfuric acid a dull blue-black solution is formed. It does not dissolve in cold aqueous alkalies, *but when warmed goes gradually into solution.*

4-Nitro-2-aceto-naphthol-1-α-naphthylhydrazone, $C_{10}H_5NO_2OHC(NNC_{10}H_8)CH_3$.—One molecule of nitroacetonaphthol was dissolved in alcohol containing a small quantity of acetic acid and to the hot solution was added one molecule of the hydrazine. The resulting deep brown solution was boiled two hours; the heavy, dark red compound which separated out was filtered from the solution, extracted with glacial acetic acid and alcohol, and dried.

Calculated for $C_{22}H_{17}N_3O_3$: N, 11.32; found, 11.03.

The dark red crystals have no melting point, but decompose when heated to a high temperature. It is soluble in acetone, benzene, and aniline, but insoluble in alcohol, glacial acetic acid, and carbon tetrachloride. Concentrated sulfuric acid gives a deep green solution. On dilution a dark green flocculent precipitate is produced. *It is insoluble in cold aqueous sodium hydroxide, but when warmed the solution is colored yellow.*

4-Nitro-2-aceto-naphthol-1-β-naphthylhydrazone, $C_{10}H_5NO_2OHC(NNHC_{10}H_7)CH_3$.—This compound was prepared like the α compound.

Calculated for $C_{22}H_{17}N_3O_3$: N, 11.32; found, 11.06.

Light, bright red body, which decomposes at 240°. It is soluble with great difficulty in glacial acetic acid, alcohol, ligroin, or benzene. With concentrated sulfuric acid the compound is decomposed, and on dilution a brown precipitate is formed. *It is insoluble in cold sodium hydroxide solution but is decomposed when the solution is heated*; the solution is colored yellow and the residue forms an oily film upon the surface.

Insolubility of β-Hydroxynaphthylaldehyde Phenylhydrazone, $C_{10}H_6OH.CH(N.NH.C_6H_5)$.—In the description of this derivative in the literature[1] no data were given in regard to its solubility in aqueous alka-

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[1] T. v. Horlacher, Dissertation, Heidelberg, 1899; Horlacher and Gatterman, *Ber.*, **32**, 286 (1899).

lies. The hydrazone crystallizes from glacial acetic acid in bright yellow, lustrous leaflets, which blacken and melt at 205°–208°. *It is insoluble in cold aqueous sodium hydroxide solution.* When warmed for some time the solution was colored slightly yellow, but even after continued boiling none of the original hydrazone could be precipitated from the alkaline filtrate. A trace of a decomposition product was obtained, but only when the alkaline solution was boiled for several hours. The compound may therefore be regarded as an alkali-insoluble naphthol.

β-Hydroxynaphthylaldehyde p-Bromophenylhydrazone, $C_{10}H_6OH.CH(NNHC_6H_4Br)$.—When equivalent amounts of the aldehyde and the hydrazine in alcoholic solution were mixed, the pale yellow reaction product began to separate from the solution almost immediately. The mixture was warmed for a short time, the product filtered off and purified by recrystallization from glacial acetic acid or from acetone.

Calculated for $C_{17}H_{13}ON_2Br$: Br, 23.16; found, 23.15.

The shining yellow crystals when pure melt with decomposition at 194°–195°. It is soluble with difficulty in alcohol, benzene, carbon tetrachloride, or chloroform, and somewhat more easily soluble in acetone, or in glacial acetic acid. *It is insoluble in boiling sodium hydroxide solution of 10% concentration.*

β-Hydroxynaphthylaldehyde Benzylphenylhydrazone, $C_{10}H_6OH.CH(NNC_7H_7C_6H_5)$.—The two substances in molecular proportions were dissolved in alcohol; 20% of glacial acetic acid was added, and the mixture warmed for half an hour on the steam bath. The product was recrystallized from glacial acetic acid, filtered, and boiled with dilute alcohol to remove traces of the acid.

Calculated for $C_{24}H_{20}ON_2$: N, 7.96; found, 8.34.

The fine, pale green crystals sinter at 151° and melt at 152°–153° without decomposition. The crystals are soluble with difficulty in alcohol, more readily in glacial acetic acid, and easily soluble in benzene. *They are entirely insoluble in boiling sodium hydroxide solution.*

All attempts to obtain an acetate of this compound, either by the use of pyridine and acetyl chloride or by acetic anhydride and fused sodium acetate, were without success.

β-Hydroxynaphthylaldehyde Benzidine, $(C_{10}H_6OH.CH)_2N_2(C_6H_4)_2$.—Two molecules of the aldehyde and one molecule of benzidine were dissolved separately in alcohol and the solutions mixed. The mixture was gently warmed and after one hour it was allowed to cool slowly. The product was purified by extraction with alcohol until the difficultly soluble residue had been freed from the soluble by-products of the reaction.

Calculated for $C_{34}H_{24}O_2N_2$: N, 5.70; found, 5.86.

A bright scarlet compound which decomposes when heated to a high temperature. It is soluble with great difficulty in the usual organic solvents; when heated with aniline or nitrobenzene it dissolves with partial decomposition and upon dilution with alcohol an impure product crystallizes out. *The pure product is insoluble in boiling 10% sodium hydroxide solution.*

β-Hydroxynaphthylaldehyde Semicarbazone, $C_{10}H_6OH.CH(NNHCONH_2)$.—This compound was prepared by the same method as the corresponding derivative of acetonaphthol, and purified by repeated crystallization from alcohol.

Calculated for $C_{12}H_{11}O_2N_3$: N, 18.34; found, 18.22.

Beautiful, shining yellow needles, which sinter and form a yellow film on the sides of the melting-point tube at 217°–218° and gradually melt with decomposition above 240°. It is soluble in alcohol, acetic acid, benzene, or ether, but insoluble in carbon tetrachloride, chloroform, or ligroin. *It is readily soluble in cold 10% aqueous sodium hydroxide solution,* and soluble with rather more difficulty in ammonia.

β-Hydroxynaphthylaldehyde Phenylhydrazone Monoacetate, $C_{10}H_6O.COCH_3.CH(N.NH.C_6H_5)$.—A mixture of 2.5 grams of the hydrazone, 12 grams of acetic anhydride, and 2.6 grams of fused sodium acetate, was heated to boiling for an hour. The excess of anhydride was decomposed by a solution of acid sodium carbonate, the crude product washed by decantation, dissolved in alcohol, decolorized by boiling with animal charcoal, and further purified by repeated crystallization from hot 60% alcohol.

Calculated for $C_{19}H_{16}O_2N_2$: N, 9.21; found, 8.94.

The long, white, silky needles melt without decomposition at 164°–165°. The acetate is insoluble in ligroin, but soluble in alcohol, benzene, methyl alcohol, and carbon tetrachloride. When heated with sodium hydroxide solution the compound slowly decomposes, giving a slight odor of phenylisocyanide.

β-Hydroxynaphthylaldehyde Azine Monoacetate, $C_{10}H_6O.COCH_3.CH.NN.CH.C_{10}H_6OH$.—Prepared by the method used for the preceding compound. The crude product was dried over potassium hydroxide, dissolved in benzene, and filtered. The residue, after evaporation, was further purified by repeated crystallization from hot alcohol.

Calculated for $C_{24}H_{18}O_3N_2$: N, 7.33; found, 7.46.

The pale yellow crystallin product melts without decomposition at 183°–185°.

β-Hydroxynaphthylaldehyde Oxime, $C_{10}H_6OH.CH.NOH$.—In an attempt to secure evidence of the presence of a quinoid oxygen in the alkali-insoluble naphthols, the phenyl hydrazone of β-hydroxynaphthylaldehyde was subjected to the continued action of hydroxylamine in the presence of hot concentrated alkali for several hours. Two compounds were obtained, the analysis of which showed that in each the oxime group had directly replaced the phenylhydrazone group. The method of preparation and separation was as follows:

A mixture containing one molecule of the phenylhydrazone suspended in alcohol, three molecules of hydroxylamine hydrochloride and nine molecules of potassium hydroxide dissolved separately in water, was boiled with a reflux condenser for four hours; the resultant clear yellow solution was poured into water and carefully neutralized with dilute hydrochloric acid, and the flocculent salmon-colored precipitate filtered out by suction. This product was further purified by dissolving in 80% alcohol and boiling with animal charcoal. The hot alcoholic solution was filtered, and on cooling fine yellow-brown needles were formed, removed by suction, and recrystallized from alcohol until the product gave the constant melting point of 148°–150°. The mother liquor contained the second (isomeric) oxime.

Calculated for $C_{11}H_9O_2N$: N, 7.48; found, 7.52.

First Oxime.—The oxime is probably the same as that obtained by Horlacher;[1] although his product had a slightly higher melting point (151°) and he describes it as rose-red instead of yellow-brown; or it is possible that the product which he secured was a mixture of the two isomers since he used acetic acid as the crystallizing agent instead of alcohol.

Second Oxime.—The mother liquor from the oxime described above on dilution gave a voluminous salmon-colored precipitate, more readily soluble in alcohol than the first oxime. The precipitate was dissolved in alcohol, boiled with animal charcoal, the filtrate diluted with two volumes of water, and the precipitate crystallized from 50% alcohol.

Calculated for $C_{11}H_9O_2N$: N, 7.48; found, 7.68.

The feathery salmon-colored crystals have a constant melting point of 158°–160°, or about ten degrees higher than that of the first oxime. The yield was approximately 30% of the total pure oxime obtained. It differs in color, crystallin form, solubility, and melting point from the first oxime.

Benzal-2-aceto-1-naphthol Tribromide, $C_{10}H_5BrOH.CO.CHBr.CHBr.C_6H_5$.—This compound was obtained by adding an excess of bromine to a solution of benzalacetonaphthol in carbon tetrachloride or in carbon disulfide. The mixture was evaporated nearly to dryness on the steam bath, and the residue redissolved in benzene and filtered. Upon addition of alcohol to the clear benzene solution the tribromide crystallized out. The same tribromide is also obtained when benzalbromoacetonaphthol is brominated.

Calculated for $C_{19}H_{13}O_2Br_3$: Br, 46.78; found: I, 46.98, II, 46.54.

Bright yellow needles, which melt at 199° without decomposition. It is soluble in carbon tetrachloride, carbon disulfide, ether, benzene,

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[1] Horlacher, Dissertation, Heidelberg, 1899.

and chloroform, and slightly soluble in alcohol. It is soluble with difficulty in a boiling 10% solution of sodium hydroxide, but *insoluble in boiling 30% aqueous sodium hydroxide solution.* When heated in an oil bath to 250° the melted mass gives off hydrobromic acid fumes in large quantities. The residue consists of a mixture of two or more derivatives which are difficult to isolate.

Piperonal-4-bromo-2-aceto-1-naphthol, $C_{10}H_5Br.OH.CO.CH.CH.C_6H_3O_2CH_2$.—A mixture of 10 grams of bromoacetonaphthol, 6 grams of piperonal, 60 grams alcohol, and 20 grams of a 40% sodium hydroxide solution was warmed on the steam bath for one hour. The color of the solution changed from green to deep red. The alkaline solution was poured into water, and the precipitate washed by decantation. The dried product was purified by extraction of the more soluble impurities by hot alcohol and hot benzene.

Calculated for $C_{20}H_{13}O_4Br$: Br, 20.16; found, 20.47.

The bright red amorphous residue has a fairly constant decomposition point of 209°–214°. It is soluble in ether and chloroform, but nearly insoluble in alcohol, benzene, ligroin, and glacial acetic acid. It is slightly soluble in boiling 10% sodium hydroxide solution, but *is insoluble in boiling 30% sodium hydroxide.* The compound dissolves in concentrated sulfuric acid with the brilliant purple color characteristic of some of the piperonal derivatives.[1]

Furfural-4-bromo-2-aceto-1-naphthol, $C_{10}H_5Br.OH.CO.CH.CH.C_4H_4O$.—This was prepared by the same method as for the piperonal derivative, except that the mixture was boiled for three hours. The precipitate thrown out when the mixture was diluted was purified by solution in benzene, filtration, and evaporation to dryness. The viscous residue was dissolved in carbon tetrachloride and upon addition of hot alcohol the pure substance crystallized out.

Calculated for $C_{17}H_{11}O_3Br$: Br, 23.32; found, 23.62.

Dark red-brown needles, melting point 154°–155°, soluble in ether, carbon tetrachloride, and benzene, but almost insoluble in alcohol. It dissolves slightly in boiling 10% sodium hydroxide solution, but *is entirely insoluble in boiling 30% alkaline solution.* The crystals dissolve readily in cold concentrated sulfuric acid, giving a blood-red solution.

p-Nitrobenzal-4-bromo-2-aceto-1-naphthol, $C_{10}H_5Br.OH.CO.CH.CH.C_6H_4NO_2$.—This compound was prepared like the furfural derivative. The resulting dark red solution was poured into a very dilute acetic acid solution, and the bright red precipitate washed by decantation. The moist mass was boiled with alcohol and ether until in solution, then filtered and allowed to stand until the ether had evaporated. An orange-

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[1] Haber, *Ber.*, 24, 617 (1891); Kostanecki, *Ibid.*, 31, 727 (1898).

red precipitate separated from solution, and was recrystallized from a mixture of ether and alcohol.

Calculated for $C_{19}H_{12}O_4BrN$: N, 3.51; found, 3.45.

Orange-red crystals, melting point 194°–195°. The compound is difficultly soluble in 10% sodium hydroxide solution, but *insoluble in 30% alkaline solution.*

Solubility of o-Hydroxyacetophenone Phenylhydrazone, $C_6H_4.OH.C(N.NH.C_6H_5)CH_3$.—In order to show that the presence of substituting groups in the benzene ring is an essential condition to alkali-insolubility, it seemed of importance to study the solubility in alkalies of the above unsubstituted compound. The *o*-hydroxyacetophenone was obtained by diazotization and subsequent saponification of *o*-aminoacetophenone according to the method employed by Friedländer.[1] A dark brown oil was obtained which was purified by distillation with steam. The oily globules were pale yellow in color and heavier than water. The aqueous distillate was extracted with ether and the ether extract dried over anhydrous sodium sulfate. After distilling off the ether the oily residue was distilled *in vacuo.* The phenylhydrazone was prepared in acetic acid solution and purified by crystallization from alcohol. The crystals are nearly white and have a constant melting point of 109°–110°. Auwers, who first prepared the compound, gives a slightly lower melting point (108°). The hydrazone is *readily soluble in dilute sodium hydroxide solution*, which confirms the statement of Tahara,[2] but it is insoluble in ammonia, and gives no color test with ferric chloride.

Acetyl-salicylaldehyde Benzylphenylhydrazone, $C_6H_4OOCCH_3.CH.N.N(CH_2C_6H_5)C_6H_5$.—The benzylphenylhydrazone of salicylaldehyde, first prepared by Minunni,[3] is soluble with difficulty in boiling 10% sodium hydroxide solution, and insoluble in cold alkalies, showing a decided effect of the benzyl group in the side chain on the solubility of the compound. It does not give a color test with ferric chloride, even after long standing. The acetylation was carried out in pyridine solution by Denninger's method.[4] The reaction mixture was allowed to stand over night at room temperature, which is important for the completion of the reaction. The solution was acidified with dilute sulfuric acid, and when free from traces of pyridine was purified by recrystallization from dilute alcohol.

Calculated for $C_{22}H_{20}O_2N_2$: N, 8.14; found, 8.40.

The acetate crystallizes in thin, white, lustrous plates, and melts at 137°–139° without decomposition.

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[1] *Ber.*, **30**, 1080 (1897).

[2] *Ibid.*, **25**, 1309 (1892).

[3] *Gazz. chim. ital.*, [2] **27**, 239 (1897)

[4] *Ber.*, **28**, 1322 (1895).

Insolubility of Benzidine-bis-salicylaldehyde, $(C_6H_4OH.CH)_2N_2(C_6H_4)_2$.—Prepared by the method of Schiff and Vanni and purified by repeated extraction of impurities with hot alcohol. The pale yellow crystals melt at 260° and are insoluble in alcohol, and only soluble with difficulty in hot benzene. It is *entirely insoluble in cold 10% sodium hydroxide solution;* even after continued boiling of the solution the compound remained undissolved, though the solution is colored slightly yellow. It is also insoluble in ammonia. When the crystals are treated with cold dilute hydrochloric acid they immediately change in color from pale yellow to deep orange; the yellow color is restored when an excess of alkali is added. When warmed for a short time with dilute hydrochloric acid the substance is hydrolyzed to its components, salicylaldehyde and benzidine hydrochloride. The *azine* of bis-salicylaldehyde was prepared by Cajar's method[2] and was found to be *readily soluble in alkalies.* It has the peculiar property of changing in color when warmed. The crystals at room temperature are pale yellow, but when warmed in the drying oven to 80°–100° become a deep orange-yellow, and return to their original state on cooling.

5-Bromosalicylaldehydephenylacethydrazoneacetate, $C_6H_3BrOOCCH_3.CH.N.N(COCH_3)C_6H_5$.—The phenylhydrazone was dissolved in pyridine and treated with an excess of acetyl chloride. Upon standing 24 hours the solution became deep red in color. The residue, after acidification, was washed with dilute acid until free from pyridine, and the resinous impurity removed by boiling the alcoholic solution with animal charcoal. The compound was precipitated on dilution, and recrystallized from 80% alcohol.

Calculated for $C_{17}H_{15}O_3N_2Br$: Br, 21.33; found, 21.34.

The purified product consists of nearly colorless crystals, which sinter at 132° and melt without decomposition at 135°–136°.

5-Bromosalicylaldehyde Azine, $(C_6H_3Br.OH.CH)_2N_2$.—A mixture of 5-bromosalicylaldehyde dissolved in alcohol and the equivalent amount of hydrazine sulfate in aqueous solution was warmed on the steam bath for half an hour, and the flocculent yellow precipitate filtered from the solution. The dried product was dissolved in boiling nitrobenzene, the solution filtered, and the filtrate diluted with alcohol. The fine, yellow crystals which formed were washed with hot alcohol and dried.

Calculated for $C_{14}H_{10}O_2N_2Br_2$: Br, 40.20; found, 39.92.

Fine, yellow needles which sinter at 301° and melt with decomposition at 305°–307°. Like the azine of salicylaldehyde previously mentioned, this compound changes in color from pale yellow to orange when warmed to 100° in a drying oven, but it resumes its original color on cooling.

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[1] *Ann.*, **258**, 374 (1890).

[2] *Ber.*, **31**, 2807 (1898).

The azine is soluble with great difficulty in the usual organic solvents, but dissolves readily in cold 10% sodium hydroxide solution, and is also soluble in ammonia. It does not, however, give a color test with ferric chloride.

Action of Light upon Hydrazones.—It was noticed that the crystallin samples of some of the hydrazones were affected by sunlight. The phenylhydrazone of salicylaldehyde when exposed to diffused sunlight changes in less than an hour from pale green to pink. The nearly white crystals of 5-bromosalicylaldehyde phenylhydrazine are equally sensitive to light, and change to a pink tint. The light yellow phenylhydrazones of acetonaphthol and bromoacetonaphthol are considerably less sensitive, but if exposed directly to sunlight they gradually turn brown. The presence or absence of air apparently does not affect the color change. F. D. Chattaway[1] has pointed out that benzaldehyde phenylhydrazone is affected by sunlight and has offered the explanation that light may cause a rearrangement of the hydrazine configuration into the azo-configuration, an hypothesis which is supported by the fact that when the hydrogen of the imide group is replaced by a phenyl or benzyl residue the compound is no longer sensitive to light. This theory is supported by our results, for the benzylphenylhydrazones of salicylaldehyde, 5-bromosalicylaldehyde, acetonaphthol, and bromoacetonaphthol, are not affected by several days' exposure to the direct rays of the sun.

Hydrolysis of Hydrazones.—When small portions of the hydrazones were boiled for some time with dilute hydrochloric acid, complete hydrolysis took place in the case of salicylaldehyde phenylhydrazone and *o*-hydroxyacetophenone phenylhydrazone, two compounds which are soluble in alkalies, while the alkaline-soluble phenylhydrazones of acetonaphthol, bromoacetonaphthol, nitroacetonaphthol, and β-naphtholaldehyde were unchanged after boiling with dilute acid for an hour or more, so that in these cases the hydrazones which are insoluble in alkalies were not hydrolyzed by boiling with aqueous acids, but all of them were decomposed when boiled with acids in presence of alcohol. The benzidine derivatives both of salicylaldehyde and of acetonaphthol were hydrolyzed however, although they are insoluble in alkalies; while the azine compounds of salicylaldehyde, acetonaphthol, and β-naphtholaldehyde remained unchanged even in presence of alcohol, in spite of the fact that the first is soluble, the second insoluble in alkalies.

Substitution in the Hydroxyl Group.—Attempts to secure evidence of the presence of the hydroxyl group by means of phenylisocyanate to form carbamates, or by means of dimethyl sulfate or methyl iodide to give the methoxyl derivatives, were unsuccessful. An attempt was made to obtain the oxime of the phenylhydrazone of acetonaphthol, but the

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[1] *J. Chem. Soc.*, 89, 462 (1906).

phenylhydrazone residue was directly replaced by the oxime group, giving the simple oxime of acetonaphthol as a product. As pointed out by Friedländer,[1] it is extremely difficult to obtain the methyl ether of the original compound, acetonaphthol, and it is probable that the protecting influence of the two ortho substituents prevented the substitutions desired.

Reaction with Ferric Chloride.—The majority of phenols in aqueous solution upon the addition of ferric chloride give a characteristic color reaction, and this is almost universal in the case of ortho derivatives.[2] Salicylaldehyde and 5-bromosalicylaldehyde give an intense violet color, and acetonaphthol and bromacetonaphthol give a deep green test. But the phenylhydrazones of the same compounds, in alcoholic solution, give only a faint yellow test; however, the solutions of the alkali-insoluble phenols on standing for a half hour or more, gradually change to a deep red-brown. The same change is brought about more quickly by heating the solution. The phenylhydrazone of salicylaldehyde does not give a color test with ferric chloride even after long standing.

CAMBRIDGE, MASS.

ON THE MAXIMUM YIELD OF AMINES BY THE REDUCTION OF ALKYL CYANIDES.

BY JITENDRA NATH RAKSHIT.

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Mendius[3] prepared alkylamines by the reduction of their cyanides with zinc dust and dilute hydrochloric acid. Siersch[4] modified the method by arranging a series of vertical tubes filled with granulated zinc, through which a mixture of nitrile, hydrochloric acid, and alcohol had to circulate. The principles involved in the improvement are the exposition of a larger surface in a shorter duration and prevention of hydrolysis by using an alcoholic medium for the reaction. It was further modified by Ladenburg,[5] who introduced alcohol and sodium for the hydrogenation.

Having had to prepare amines in quantities from the nitriles,[6] Mendius', Siersch's and Ladenburg's methods have been successively tried but the bases produced have been always found to be considerably contaminated with ammonia. By the former two only nominal quantities of amines were obtained and by the latter some amines were produced. The yield was much below the theoretical. It had been observed that on increas-

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[1] *Ber.*, 28, 1949 (1895).

[2] Wegscheider and Bittner, *Monatsh.*, 21, 650 (1900).

[3] *Ann.*, 121, 229.

[4] *Ibid.*, 144, 139.

[5] *Ber.*, 19, 1783.

[6] Ray and Rakshit, *Trans. Chem. Soc.*, 99, 1471; 101, 141.