nitrate mixed with nitroglycerin by the optical method and by calculation from total nitrogen was afforded by the examination of a manufacturer's sample of such a mixture, the method of preparation of which was not known to the authors. By the optical method, the sucrose nitrate was determined as 15.52%; calculated from the nitrogen determination the percentage of the sucrose nitrate was 16.86. The mixture probably contained other constituents, possibly some stabilizing material which would affect the results by the latter method.

Summary.

1. The crude product of the nitration of sucrose under the conditions above described is a tough, viscous, semi-transparent mass, which can be pulverized on cooling to hardness. It has no definite solidification temperature and is unstable above 30°. It contains an average nitrogen content of 15%, and has an average specific rotatory power of 56.66°.

2. Sucrose octanitrate has been separated from the crude nitration product and identified as well-defined crystals belonging to the orthorhombic or monoclinic system, more probably the latter. It melts at 85.5° and is very stable. Nitrogen and molecular-weight determinations gave values which are practically identical with those calculated for sucrose octanitrate. Its specific rotatory power was determined as 56.05°.

3. Sufficient data have been accumulated for a limited application of the polariscope to the analysis of explosive mixtures containing nitrated sucrose, and these form a basis for the further development of the method.

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ALKALI-INSOLUBLE PHENOLS.

BY ROGER ADAMS.[1]

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Solubility in aqueous alkalies is a general property one expects all phenols to possess. Nevertheless, many of them which do not have this property have been described. Some of these appear to be isolated examples while others seem to fall into classes such as the pseudo phenols of Zincke, the *o*-azophenols studied by Liebermann and others and the phenylhydrazones of certain *o*-hydroxyaldehydes and ketones investigated by Anselmino, Torrey and the author of this paper. The object of the present

[1] The subject of this investigation was suggested by H. A. Torrey, and the work in this field was begun under his direction and published in *Ber.*, **43**, 3227 (1910). The continuation of the research, however, which is described in this publication was deprived of the benefit of his supervision by his early death in February, 1910. Although the views put forward in this communication do not agree with those held by Dr. Torrey, I feel that anything of value which may be contained therein is due to his encouragement and guidance in the beginning.

investigation was to study more thoroughly the phenylhydrazones of the *o*-hydroxyaldehydes and ketones, to determine the structure characteristic of compounds of this type which are insoluble in alkalies, and finally to find an explanation of this insolubility.

From this investigation the following conclusions can be drawn:

(1) The introduction of any atom or group of atoms into any part of the molecule of a phenylhydrazone of an *o*-hydroxyaldehyde or ketone causes the solubility of the resulting substance in 10% aqueous alkali to decrease. Each of the various substituting groups has a different effect on the molecule, so that phenols with all gradations of alkali insolubility may be produced. Certain nitro derivatives are apparent exceptions to this generalization but each nitro compound showing this anomaly is capable of aci-nitro group formation, thus producing alkali-soluble compounds on account of this latter arrangement and not on account of the hydroxyl group.

(2) The various explanations which have already been offered for the alkali insolubility of these compounds are unsatisfactory.

(3) A very simple explanation, namely, that the insolubility in alkali is due to the extreme insolubility of these phenols in water, coupled with their very slight dissociation agrees with all the facts available. This is exactly the way the insolubility in alkali of any very insoluble and slightly dissociated acid would be explained.

In the following pages will be described: (1) the previous work which has been done on this particular group of alkali-insoluble phenols; (2) a comparison of the effects of the various groups on the insolubility of the phenylhydrazones of *o*-hydroxyaldehydes and ketones; (3) a review of the previous explanations offered for the alkali insolubility of these substances; (4) the explanation advanced from the results of this research together with the experimental facts substantiating it.

I. Anselmino[1] discovered that the phenylhydrazones of *p*-hydroxybenzaldehyde and its derivatives are soluble in aqueous alkali, that the phenylhydrazone of salicyl aldehyde is also soluble but that the phenylhydrazones of the mono-, di-, and trimethyl derivatives of salicyl aldehyde show various gradations of alkali insolubility. He concluded that to have alkali insolubility in these compounds, it is necessary to have the phenylhydrazone of the aldehyde group ortho to the hydroxyl group and to have a carbon substituting group in the phenol ring at the same time. The latter condition has more effect on the insolubility than the former for the phenylhydrazone of salicyl aldehyde is perfectly soluble in alkali. Anselmino, however, did not explain the insolubility. Torrey[2]

[1] *Ber.*, **35**, 409 (1902).

[2] THIS JOURNAL, **29**, 77 (1907); **30**, 836 (1908); **31**, 1322 (1909); *Ber.*, **43**, 3227 (1910); THIS JOURNAL, **35**, 426 (1913).

investigated the phenylhydrazones of the *o*-hydroxyketones in the benzene and naphthalene series, most of which possess aqueous alkali-insolubility. From the behavior of over 40 compounds, he concluded just as Anselmino had that the hydroxyl group and large side chains must be ortho to each other and that there must also be a carbon-substituting group in the ring. Torrey discussed various possible explanations for the insolubility and showed conclusively that of those he suggested only that of tautomerism between quinoid and phenol modifications is at all satisfactory. These will be considered later.

II. In the present research, 10% aqueous sodium hydroxide was used in every case to test the solubility, and particular care was taken to distinguish between the solubility of the phenols in cold, warm, hot or boiling alkali. After preparing a large number of various phenylhydrazones of different hydroxyaldehydes and ketones, it was possible to show that the conclusions of the previous investigators are not wholly correct. It was found that the substitution of a group containing carbon in the phenol ring is not absolutely necessary to produce alkali insolubility, and that a large number of alkali-insoluble phenols of this type can be prepared which have no substituting group at all in the phenol ring. A study of the relative effect on the solubility, of various groups substituted in the phenol residue and phenylhydrazone residue was carefully made and in the following table are included some of the compounds from which conclusions have been drawn in regard to this point:

TABLE I.—SOLUBILITY EFFECT.

	Soluble in Cold Alkali.
Hydrocarbon substitution..	$C_6H_4(OH)^1(CHNNHC_6H_5)^2$
	$C_6H_4(OH)^1[C(CH_3)NNHC_6H_5]^2$
Halogen substitution.....	$(Br)^4C_6H_3(OH)^1(CHNNHC_6H_5)^2$
Nitro substitution.....	$(NO_2)^4(CH_3)^6C_6H_2(OH)^1(CHNNHC_6H_5)^2$
	$(NO_2)^6(CH_3)^4C_6H_2(OH)^1(CHNNHC_6H_5)^2$
Unsubstituted hydrazine derivatives.....	$(CH_3)^4C_6H_3(OH)^1(CHNNH_2)^2$
	$(CH_3O)^5C_6H_3(OH)^1[C(CH_3)NNH_2]^2$
Azine derivatives.....	$[(CH_3)^4C_6H_3(OH)^1(CH)^2]_2N_2$
	$[C_{10}H_6(OH)^1(CH)^2]_2N_2$
	Soluble in Warm Alkali.
Hydrocarbon substitution..	$(CH_3)^4C_6H_3(OH)^1(CHNNHC_6H_5)^2$
	$C_6H_4(OH)^1[CHNNHC_6H_4CH_3(o \text{ or } p)]^2$
Halogen substitution.....	$(Br_{2\text{-}6})C_6H_2(OH)^1(CHNNHC_6H_5)^2$
Nitro substitution.....	$(NO_2)^4(CH_3O)^5C_6H_2(OH)^1[C(CH_3)NNHC_6H_5]^2$
	$(NO_2)^4(Br)^6(CH_3O)^5C_6H(OH)^1[C(CH_3)NNHC_6H_5]^2$
	$(NO_2)^2C_6H(OH)_2{}^{1\cdot3}[C(CH_3)NNHC_6H_5]_2{}^{4\cdot6}$
	$(CH_3O)^5C_6H_3(OH)^1[C(CH_3)NNHC_6H_4NO_2(p)]^2$
	$(Br)^4(CH_3O)^5C_6H_2(OH)^1[C(CH_3)NNHC_6H_4NO_2(p)]^2$

	Soluble in Hot Alkali.
Hydrocarbon substitution..	$(CH_3O)^5C_6H_3(OH)^1[C(CH_3)NNHC_6H_5]^2$
	$C_6H_4(OH)^1[CHNC_6H_4COCH_3(p)]^2$
Halogen substitution.....	$(Br)^6(CH_3)^4C_6H_2(OH)^1(CHNNHC_6H_5)^2$
	$C_6H_4(OH)^1[CHNNHC_6H_4Br(p)]^2$
Hydrocarbon substitution..	$(CH_3)_2^{4\cdot6}C_6H_2(OH)^1(CHNNHC_6H_5)^2$
	$C_6H_4(OH)^1[CHNC_6H_4COC_6H_5(p)]^2$
	Insoluble in Boiling Alkali.
Halogen substitution.....	$C_6H_4(OH)^1[CHNNHC_6H_2(Br)_3^{2\cdot4\cdot6}]^2$
	$(Br)^4(CH_3O)^5C_6H_2(OH)^1[C(CH_3)NNHC_6H_5]^2$
	$(Br)^4(CH_3O)^5C_6H_2(OH)^1[C(CH_3)NNHC_6H_4Br(p)]^2$
	$(CH_3O)^5C_6H_2(OH)^1[C(CH_3)NNHC_6H_4Br(p)]^2$
	$(CH_3O)^5C_6H_2(OH)^1[C(CH_3)NNHC_6H_2(Br)_3^{2\cdot4\cdot6}]^2$
	$(Br)^4(CH_3O)^5C_6H_2(OH)^1[C(CH_3)NNHC_6H_2(Br)_3^{2\cdot4\cdot6}]^2$
Nitro substitution.....	$(CH_3O)^5C_6H_3(OH)^1[C(CH_3)NNHC_6H_4NO_2(o \text{ or } m)]^2$
Imid substitution.....	$(Br)_2^{4\cdot6}C_6H_2(OH)^1[CHNN(COCH_3)C_6H_5]^2$
	$C_6H_4(OH)^1[CHNN(CH_2C_6H_5)C_6H_5]^2$
	$(Br)_2^{4\cdot6}C_6H_2(OH)^1[CHNN(COC_6H_5)C_6H_5]^2$
Azine derivatives.....	$[(CH_3O)^5C_6H_3(OH)^1(C(CH_3))^2]_2N_2$
	$[(CH_3)^4C_6H_3(OH)^1(C(C_6H_5))^2]_2N_2$

From the table it is evident that a methyl group or in general a group containing carbon whether it is substituted in the phenol ring or in the side chain, has a great influence on the solubility in alkali of the resulting compounds. The effect is slightly greater in the phenol ring than in the side chain. A comparison of the more soluble phenylhydrazone of salicyl aldehyde with the less soluble phenylhydrazones of *p*-homosalicyl aldehyde, dimethylsalicyl aldehyde and paeonol illustrates these facts very well. Torrey pointed out that aniline derivatives of certain *o*-hydroxyaldehydes and ketones have the same solubility in alkali as the phenylhydrazine derivatives, and he prepared a number of the substituted aniline compounds, of which the examples in the table indicate the varied nature of the substituting group which may cause alkali insolubility.

A bromine atom although having less influence than the groups containing carbon nevertheless has some effect, as is shown by comparing the phenylhydrazone of paeonol with the less soluble phenylhydrazone of bromopaeonol, the phenylhydrazone of *p*-homosalicyl aldehyde with the less soluble phenylhydrazone of bromo-*p*-homosalicyl aldehyde, or the phenylhydrazone of bromosalicyl aldehyde with the less soluble phenylhydrazone of dibromosalicyl aldehyde. In the side chain, however, the effect is even more noticeable; the phenylhydrazones of salicyl aldehyde and paeonol are much more soluble than the *p*-bromophenylhydrazone derivatives, and these latter compounds are much less soluble than the corresponding compounds with the halogen in the phenol ring.

When a nitro group is substituted in the phenol ring in the ortho or para position to the hydroxyl group, the solubility in alkali is increased.

A nitro group in the para position of the phenylhydrazone residue produces the same effect. At first this appears directly contrary to what might be expected, but on consideration of the possibility of the rearrangement of nitrophenols as well as of *p*-nitrophenylhydrazones to form aci-nitro compounds readily soluble in alkali, this increase in solubility can be easily explained and will be considered in more detail later. Where there is no tendency for aci-nitro groups to form, as in the meta and ortho nitrophenylhydrazones, the nitro group has the same effect as other groups and increases the insolubility in alkalies. No compound with a nitro group meta to the hydroxyl was prepared but it would probably show increased alkali insolubility.

A comparison of the phenylhydrazones of *p*-homosalicyl aldehyde and paeonol with the hydrazones of the same compounds, the former being insoluble and the latter soluble in alkali, shows conclusively that a large group like the phenyl in the hydrazone residue is absolutely necessary for production of alkali insolubility.

A comparison of the azines of the hydroxyaldehydes with the azines of the hydroxyketones shows the marked effect of a methyl or phenyl radical attached to the carbon atom holding the phenylhydrazone residue, as compared with a hydrogen atom. The azines of *p*-homosalicyl aldehyde or *β*-naphthyl aldehyde are perfectly soluble in cold alkali; the azines of paeonol and methyl-5-hydroxy-2-benzophenone are insoluble in boiling alkali.

Finally a group substituted on the imid nitrogen has a decided influence on the solubility in alkali. The benzylphenylhydrazone of salicyl aldehyde or the acetyl and benzoylphenylhydrazones of dibromosalicyl aldehyde are much more insoluble than the corresponding unsubstituted phenylhydrazones.

The general conclusion may be drawn from all these results that if any atom or group of atoms excepting one which may itself independently produce alkali solubility is introduced into any part of the molecule of the phenylhydrazone of an *o*-hydroxyaldehyde, a substance of lower solubility in 10% aqueous alkali results. As might be expected, different groups have different effects on the solubility, as does also the same group substituted in different parts of the same molecule.

III. A number of suggestions as to the cause of alkali insolubility of these phenols have been offered. Torrey[1] has discussed them in detail, but for completeness they will be reviewed very briefly here and a few of the principle objections to each will be given.

1. Secondary condensation between the imid nitrogen of the phenylhydrazone residue and the hydroxyl group is impossible because analysis shows that no water has been split out.

[1] THIS JOURNAL, **29**, 77 (1907); **30**, 836 (1908).

2. Internal salt formation between the oxygen of the hydroxyl group and either of the two nitrogen atoms of the phenylhydrazone residue is out of the question, because the unsubstituted hydrazones of these hydroxy aldehydes and ketones, although containing a much more basic nitrogen atom and therefore possessing a greater tendency to form salts with the phenol group, are soluble in alkalies, whereas the phenylhydrazones, with less basic nitrogen and therefore less tendency toward salt formation, are insoluble in alkali. Moreover, the substitution of negative groups in the phenylhydrazone residue decreases the basicity of the nitrogen, but in spite of this greatly increases the insolubility in alkalies.

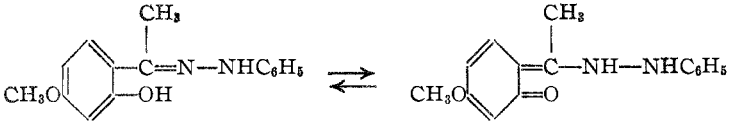
3. The formation of quadrivalent oxygen by the oxygen of the hydroxyl group and the hydrogen of the imid group is very unlikely since quadrivalent oxygen is always basic and would have no tendency to form a salt with a basic nitrogen atom. In addition it may be said that oxonium compounds are unstable, whereas all of these alkali-insoluble phenols are extremely stable.

4. Repression of the acid nature of the phenols cannot be the explanation of the insolubility, for negative groups of various kinds when introduced into the molecules do not cause these phenols to become more soluble but less soluble in alkali. The hydrazones of these *o*-hydroxyaldehydes and ketones are much more basic than the phenylhydrazones but are completely soluble in alkali while the latter are completely insoluble. Many other examples of a similar nature might be cited.

5. An explanation for the insolubility which was not suggested by Torrey, is that of steric hindrance. This is not satisfactory, however. It is difficult, for instance, to see how a group para to the hydroxyl in the phenol ring or particularly in the para position of the phenylhydrazone residue would have such a marked influence on the activity of the hydroxyl group. The phenylhydrazone of salicyl aldehyde is soluble but the phenylhydrazone of *p*-homosalicyl aldehyde or the *p*-bromophenylhydrazone of salicyl aldehyde are both insoluble. The examples of steric hindrance recorded in the literature in practically every case involve the non-reactivity of a group due to the close proximity of other atoms or groups. In these alkali-insoluble phenols, however, almost any kind of group in any part of the molecule has the same effect.

6. Torrey[1] considered carefully the possibility of keto-enol tautomerism in these compounds with the idea that in these phenols chiefly the quinoid form existed and therefore the substances were insoluble in alkalies. Although not coming to a final conclusion that this was correct, he favored this explanation. As an example the phenylhydrazone of paeonol may be given.

[1] *Loc. cit.*



His arguments were as follows: first for the quinoid structure:

(*a*) These insoluble phenols were in general highly colored. Of 20 which he studied, only two were nearly white, all the rest being from yellow to deep red.

(*b*) These compounds did not react with phenyl isocyanate to form urea derivatives nor with sodium hydroxide and dimethyl sulfate to give ethers, indicating that no hydroxyl group was present.

(*c*) These substances hydrolyzed only with great difficulty with aqueous hydrochloric acid, showing the possibility of a single bond between the carbon of the aldehyde or ketone group and the nitrogen of the phenylhydrazone residue, a state such as would exist provided quinoid structure was present.

(*d*) The insolubility in alkali itself indicated the non-existence of a hydroxyl group and therefore the probability of quinoid structure.

No direct chemical evidence of the quinone oxygen could be obtained, however; but this fact Torrey explained by assuming that the large neighboring group had greatly reduced its reactivity.

For the phenol structure, his arguments were as follows:

(*a*) The sodium salts could be formed if the phenols were treated with an alcoholic solution of sodium alcoholate and then evaporated to dryness.

(*b*) These phenols formed acetates by the action of acetic anhydride. Diacetates could also be produced in some cases showing that both the hydrogen of the hydroxyl and the hydrogen of the imid nitrogen had been replaced.

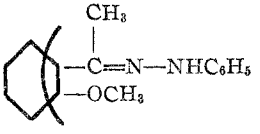
(*c*) Alcoholic hydrochloric acid readily hydrolyzed these substances to the hydroxyketone or aldehyde and phenylhydrazine or a phenylhydrazine derivative.

On the basis of these data, Torrey considered that these compounds existed in a state of equilibrium, a balanced action between the quinoid and phenolic forms. He believed the quinoid form to be more stable, but in solution or in the presence of certain reagents isomerization to the phenol form takes place. In this way, the action of the compounds toward aqueous hydrochloric acid, toward aqueous sodium hydroxide, toward sodium alcoholate or toward the other reagents could be explained.

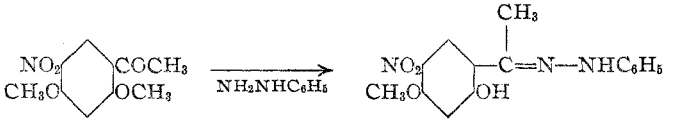
IV. In studying the possible ways to account for the alkali insolubility, it seemed somewhat doubtful whether the quinoid-phenol equilibrium explanation was satisfactory, particularly since no direct evidence of the quinoid form had been obtained. The experiments indicating the phenol form were conclusive but a further consideration of the arguments for the

quinoid form seemed necessary. The results of a study of the compounds prepared in this present research show that the depth of color does not by any means go hand in hand with alkali insolubility, or, in other words, according to Torrey, with the quinoid formation. Several compounds have been made that are perfectly white yet exceedingly insoluble in boiling alkali. As examples may be mentioned the tribromophenylhydrazones of paeonol, bromopaeonol and salicyl aldehyde, the *o*-tolylhydrazone and the *p*-bromophenylhydrazone of salicyl aldehyde. Moreover, many phenols of this type are colored yet wholly soluble in alkali. Thus the phenylhydrazone of salicyl aldehyde is yellow and completely soluble in the cold; the bromophenylhydrazone and the tribromophenylhydrazone of salicyl aldehyde are white and insoluble in alkali. There seems, therefore, to be little connection between the color and alkali insolubility and therefore between the color and quinoid formation.

The non-formation of methyl ethers by the action of dimethyl sulfate and sodium hydroxide was the second argument against the phenol modification. In this work, further study along this line gave interesting results. Attempts were made to prepare the methyl ethers of the phenylhydrazones of the *o*-hydroxyaldehydes and ketones by first making the methyl ethers of the *o*-hydroxyaldehydes or ketones and then condensing these derivatives with phenylhydrazine. Surprising results were obtained. Neither the methyl ether of paeonol nor that of bromopaeonol will condense with phenylhydrazine. This immediately leads to the conclusion that the grouping



is not capable of existence or certainly cannot be formed at all readily. One of the substances of this type was later found in the literature,[1] but the preparation could not be repeated. A study of the methylether of nitropaeonol confirms the conclusions arrived at in this research. By treatment of an alcoholic solution of the methylether of nitropaeonol with an alcoholic solution of phenylhydrazine, a phenylhydrazone is immediately produced which, however, is the phenylhydrazone of nitropaeonol and not of the methylether. During the reaction the methylether has been split down.



This is an exceptional reaction for an ether, one of a class of compounds

[1] *Ann.*, 360, 347 (1909).

which is generally very stable indeed. The molecule has actually broken in order to allow the phenylhydrazine to react with the ketone, thus showing that the above-mentioned combination of groups is an unstable one and difficult to form. It is thus evident that steric hindrance is preventing the formation of these ethers by the ordinary methods and that the assumption that the presence of quinoid grouping is the real cause is quite unnecessary. The non-reactivity of phenyl isocyanate may be explained in the same way.

A third argument advanced by Torrey for the quinoid structure was the difficulty with which the substances are hydrolyzed by aqueous hydrochloric acid. This indicated to him that the nitrogen and carbon might be united by a single bond, due to quinoid formation, thus producing a structure which would not be easily hydrolyzed. Further hydrolysis experiments have been made in the present research and it has been found that the insolubility of these phenols in alkali corresponds exactly to the difficulty with which they are hydrolyzed by aqueous hydrochloric acid. Thus there is a distinct increase in insolubility in alkalies as well as a distinct decrease in the rate of hydrolysis with aqueous hydrochloric acid as one goes from the first to the last of the following series of substances: the *o*-tolylhydrazone of salicyl aldehyde, the phenylhydrazone of *p*-homosalicyl aldehyde, the phenylhydrazone of paeonol, and, finally, the *p*-bromophenylhydrazone of *p*-homosalicyl aldehyde. It seems improbable, if the reason for slow hydrolysis is due to the quinoid rearrangement, causing a single bonded carbon-nitrogen linkage, that the various phenols would show such a wide degree of variation in their reactivity with aqueous hydrochloric acid. Torrey found that hydrolysis took place in every case if alcoholic hydrochloric acid was used and he explained this by saying that the enol form had been produced in alcoholic solution. Experiments were carried out in this research with aqueous hydrochloric acid to which a few drops of alcohol had been added. Results show that under these conditions the relative rate of hydrolysis of any of the insoluble phenols remains the same but the actual amount of hydrolysis increases about equally in each substance. This leads to the conclusion that the solubility in water in the first experiments and in the very dilute alcohol in the second experiments plays a very significant part in the rate of hydrolysis. It is well known that phenol itself is readily soluble in water, the cresols less soluble, the xylenols still less soluble and pseudo cumenol or tribromophenol practically insoluble in water. In the same way salicyl aldehyde, *p*-homosalicyl aldehyde, and paeonol are only very slightly soluble in water. In other words, an increase of groups in the molecule increases the insolubility of a phenol in water. The same holds true undoubtedly for the phenols studied in this research. The phenylhydrazone of *p*-homosalicyl aldehyde, an insoluble phenol which

is hydrolyzed in 15 minutes in aqueous hydrochloric acid, barely turns water turbid after heating to boiling and allowing to cool, the *p*-bromophenylhydrazone of *p*-homosalicyl aldehyde which does not hydrolyze completely in aqueous hydrochloric acid in an hour, does not turn water turbid at all under the same conditions. This shows that the rate of hydrolysis is associated to some extent with the solubility in water. The solubility in water of the much more complex phenols might be predicted as being extremely small and consequently the slowness of hydrolysis in aqueous hydrochloric acid could be foreseen. If alcohol is added, the solubility of the compounds is greatly increased, causing the substances to enter the medium of reaction and consequently to hydrolyze readily. It therefore seems sufficient to explain the difference in speed and the slowness in speed of hydrolysis of these compounds by the difference in solubility rather than to assume that it is due to the presence of quinoid structure.

The foregoing discussion of Torrey's arguments for quinoid-phenol tautomerism shows conclusively that the evidence for quinoid structure of these substances is so weak that a general explanation by this means is not at all satisfactory.

The following additional experiments on these insoluble phenols were carried out. To determine quantitatively the solubility of some of these substances in water, the following tests were made: Three typical phenols were selected, the phenylhydrazone of *p*-homosalicyl aldehyde which was soluble in warm to hot alkali, the phenylhydrazone of paeonol which dissolved in hot to boiling alkali, and finally the phenylhydrazone of bromoacetonaphthol which was insoluble even in boiling alkali. Each was tested in succession by shaking thoroughly with 100 cc. of distilled water at 20° for 15 minutes, filtering and evaporating the filtrate to dryness in a platinum dish in a sulfuric acid desiccator. These experiments were then repeated using 100 cc. of boiling water, filtering and evaporating to dryness in the same way. No residue is obtained upon evaporation of the water when the solubility tests are carried out with cold solvent. When the higher temperature is used, however, there is a residue of 0.0025 g. from the phenylhydrazone of the *p*-homosalicyl aldehyde, 0.0018 g. from the phenylhydrazone of paeonol and 0.0002 g. from the phenylhydrazone of bromoacetonaphthol. The results show that the compounds are extremely insoluble in cold water, more soluble in hot, and that the relative solubility in hot water corresponds to the relative solubility in aqueous alkali.

Many of these phenols, as has been shown, are soluble in warm, some in hot or boiling alkali, although all are entirely insoluble in the cold. It is always observed, however, that on cooling the hot solution of these phenols the free phenols and never the sodium salts separate.

These insoluble phenols when treated with alcoholic sodium hydroxide always dissolve in the cold as well as at a higher temperature. It was noted, however, that certain of the phenols which are only slightly soluble in the amount of alcohol used for testing, dissolve readily in the same amount when sodium hydroxide is present, indicating that a chemical reaction has probably taken place.

A study of the sodium salts of these phenols was made. Two typical ones were chosen, the sodium salt of the phenylhydrazone of paeonol and the sodium salt of the phenylhydrazone of bromoacetonaphthol. These salts were prepared by dissolving the compounds in an absolute alcohol solution of one molecule of sodium ethylate and then evaporating to dryness in a vacuum desiccator. They were tested with the following results: On treatment either with cold water or with hot water the free phenols in both cases separate immediately, indicating instant hydrolysis; and upon heating, the solids do not go into solution. Treatment with 1% cold sodium hydroxide causes immediate hydrolysis in both cases; if 1% hot sodium hydroxide is used, however, there is a partial solution in the case of the phenylhydrazone of paeonol but none in the case of the phenylhydrazone of the bromoacetonaphthol. Treatment with 10% cold sodium hydroxide gives complete hydrolysis in both cases; but if the sodium hydroxide is hot, the sodium salt of the phenylhydrazone of the paeonol remains in solution while the sodium salt of the phenylhydrazone of bromoacetonaphthol hydrolyzes, as before, with the separation of the free phenol. Finally, treatment with cold or hot alcohol gives complete solution in all cases. These results are actually what would be obtained from any salt made up of a very weak acid and a strong base provided the acid is extremely insoluble in water.

With these new experiments, together with those carried out by Torrey, there can be given a simple explanation of alkali insolubility of these phenols. Because they are very weak acids and are very insoluble in water, the phenylhydrazones of the *o*-hydroxyaldehydes and ketones are insoluble in aqueous alkali. This is what would be expected of any insoluble, slightly hydrolyzed acid. If a positive or negative atom or group be introduced into the molecule, two effects will influence the nature of the product; first, the increase in insolubility in water due to the increased size of the whole molecule, which results in the increased insolubility in alkali; second, an increase or decrease in the acidity of the whole molecule depending upon the nature and position in the molecule of the atom or group introduced, which results in a decrease or an increase, respectively, in the insolubility in alkali. Thus observation of the compounds studied in this investigation has shown that the introduction of a bromine atom which is negative in nature decreases slightly the solubility in aqueous alkali of the resulting molecule. This is due to the fact that

the bromine causes the compound to become less soluble in water and therefore less soluble in aqueous alkali. The effect thus produced more than offsets the possible increase of solubility in alkali due to increased acidity of the molecule. According to this theory, the substitution of a methyl group, which is positive in nature, for the bromine atom might be expected to cause a greater increase in insolubility in alkali than would be produced by the bromine atom. This is because the two effects on the molecule are additive. The methyl group, by increasing the size of the molecule, increases the insolubility of the compound in water and therefore the insolubility in alkali; at the same time it decreases slightly the acidity of the molecule, thus increasing the insolubility in alkali. Two very good examples may be cited in comparing the mono- and dibromo-derivatives of the phenylhydrazone of salicyl aldehyde with the corresponding methyl-derivatives. The monobromo- is completely soluble in cold alkali, the dibromo- slowly soluble in cold alkali while the monomethyl-derivative is soluble only in warm to hot alkali and the dimethyl- slowly soluble in boiling alkali.

All the other properties of these phenols thus far studied can be explained according to this theory. The chemical reactions of the hydroxyl group described by Torrey are those of normal phenols. The difficulty with which the substances hydrolyze with aqueous hydrochloric acid and the ease with which they hydrolyze in alcoholic hydrochloric acid may be explained simply from the relative solubility of the phenol in the solvent. The fact that some of the phenols dissolve in hot alkali but separate again upon cooling means that the rise in temperature of the solvent increases greatly the solubility of the free phenol so that the total amount of sodium salt to give enough free phenol by hydrolysis to saturate the hot solution is large and therefore solution takes place; when cooling, the solubility of the free phenol decreases so that the solubility in alkali is less. The various gradations of alkali solubility of the different phenols can be readily understood because they vary with the solubility of the phenol in water. Torrey found that certain of the phenols did not give a color with ferric chloride solution in the cold but readily gave one on warming. This can also be explained by the relative solubility of the phenol in hot and cold water.

It may be suggested that probably many, although not all of the phenols appearing in the literature which are alkali-insoluble, such as Zincke's pseudo phenols have this property for the same reason as the phenylhydrazones of the *o*-hydroxyaldehydes and ketones.

Solubility in Alkali of Various Nitro Derivatives.

The fact has already been mentioned that the substitution of a nitro group in certain positions in the phenylhydrazones of the *o*-hydroxy aldehydes and ketones causes the resulting molecules to be more soluble in alkali instead of less soluble, as might be expected. Two types of nitro

compounds were studied, those having the nitro group ortho and para to the hydroxyl and those having the nitro in the ortho, meta or para positions of the phenyl group of the phenylhydrazone side chains. When the group is ortho or para to the hydroxyl, in every case a substance is produced much more soluble in the alkali than the unsubstituted compound; for example, the phenylhydrazone of paeonol is soluble in warm to hot alkali but the nitro derivative is soluble in cold alkali; if the original compound is soluble only in hot to boiling alkali, the nitro derivative will then generally be soluble in cold to warm alkali.

This increase in solubility can be understood from a study of the work by Hantzsch[1] on the nitrophenols. He has shown that these compounds are tautomeric and may exist in two modifications, the normal and aci-form. Since the latter is the stronger acid, neutralization with alkali under ordinary conditions gives the sodium salt of this form. The alkaline solutions are always more deeply colored than the nitrophenols themselves and this is true of the nitro compounds investigated in this research. Although the nitro group, by increasing the size of the molecule undoubtedly diminishes greatly the solubility in water, it does not decrease the solubility in alkali. This is because the increased acidity of the aci-nitro form, the salt of which hydrolyzes much less than the normal phenol salt produces an effect on the solubility in alkali which more than offsets that caused by increasing the size of the molecule.

The *m*-nitrophenols do not rearrange in the same way as do the ortho and para derivatives. Unfortunately a *m*-nitro compound of these insoluble phenols was not prepared but it seems probable that this group position would decrease the solubility of the resulting molecule and not increase it as is the case with the ortho and para substitution.

In the phenyl group of the phenylhydrazone side chain the nitro group has different effects depending on its position. The *o*- and *m*-nitro compounds cause the resulting substances to be less soluble in alkali. This is what would be expected. The para compounds, however, are much more soluble in alkali than the unsubstituted derivatives. This peculiarity of the para compounds is made clear by the work of Bamberger,[2] who found that the *p*-nitrophenylhydrazones in general rearranged to form aci-nitro compounds very readily, thus producing the property of aqueous alkali solubility. In the same way the *p*-nitrophenylhydrazones prepared in this investigation very probably dissolve in aqueous alkali on account of the nitro group and do not depend on the hydroxyl group in the benzene ring for this property.

In conclusion it is sufficient to say that a nitro group in the ortho or para position to the hydroxyl or in the para position of the benzene ring

[1] *Ber.*, **39**, 1084, 3072, 4237 (1906); **40**, 1523, 1556 (1907).

[2] *Ibid.*, **29**, 1829 (1896); **32**, 1806, 1810 (1899).

in the phenylhydrazone residue renders the resulting molecule more soluble in alkali than the unsubstituted compound. This solubility is due in each case to aci-nitro group formation, and therefore the apparent abnormality is not due to the phenol group itself.

EXPERIMENTAL PART.

Derivatives of Paeonol.

Paeonol, 2-Hydroxy-4-methoxyacetophenone, $C_6H_3(OH)(OCH_3)(COCH_3)$.—The paeonol[1] used in this research was made in large quantities by the following method: To 100 g. of resacetophenone was added just enough cold 10% sodium hydroxide solution to dissolve it by shaking, then 83 g. of dimethyl sulfate; the mixture was heated to a temperature of about 90° and finally shaken for several minutes. A small amount of alkali was then added and the heating and shaking repeated. The solution was acidified with hydrochloric acid and extracted with benzene, the benzene solution dried, the solvent distilled off and the resulting paeonol distilled in a vacuum. Large, transparent crystals melting at 50° were obtained in a yield of 70% to 75%.

Paeonol Phenylhydrazone, $C_6H_3(OH)(OCH_3)[C(NNHC_6H_5)CH_3]$, prepared by the method described by Tiemann,[2] formed pale yellow needles, melting at 108°. The substance was soluble in hot alkali.

Paeonol Hydrazone, $C_6H_3(OH)(OCH_3)[C(NNH_2)CH_3]$.—One molecule of paeonol was dissolved in alcohol, a slight excess over one molecule of hydrazine hydrate was added, and the mixture warmed gently for a few minutes. A small amount of the yellow, insoluble azine was filtered off and the filtrate diluted with water. White, flaky crystals appeared which were filtered at once to prevent them from turning yellow, and then quickly dried.

Subst., 0.1699 g.; N, 22.4 cc.; 768 mm., 16.0°.
Calc. for $C_9H_{12}O_2N_2$: N, 15.5. Found: 15.8.

From dilute alcohol white plates were obtained, melting at 73 to 75°, which on exposure to light quickly turned yellow and were readily soluble in common organic solvents. The compound was soluble in cold alkali.

Paeonol Azine, $[C_6H_3(OH)(OCH_3)(CCH_3)]_2N_2$.—Two molecules of paeonol and one molecule of hydrazine hydrate were refluxed in alcohol solution for two hours. The azine separated out.

Subst., 0.1799 g.; N, 13.4 cc.; 762 mm., 17°.
Calc. for $C_{18}H_{20}O_4N_2$: N, 8.5. Found: 8.8.

From glacial acetic acid fine, lemon yellow crystals melting 226 to 227° were obtained. The compound was insoluble in boiling alkali.

Paeonol 2,4,6-Tribromophenylhydrazone, $C_6H_3(OH)(OCH_3)[C(NNHC_6H_2Br_3)CH_3]$.—Equal molecules of tribromophenylhydrazine and paeonol

[1] *Ber.*, **24**, 2460, 2847 (1891); **25**, 252 (1892); THIS JOURNAL, **29**, 77 (1907).
[2] *Ber.*, **24**, 2854 (1891).

were refluxed two hours in alcohol solution. The crude product separated on cooling.

Subst., 0.1596 g.; AgBr, 0.1857 g.
Calc. for $C_{15}H_{12}O_2N_2Br_3$: Br, 48.68. Found: 48.95.

From alcohol white needles melting at 162° were obtained. The compound was insoluble in boiling alkali. This substance must be heated to between 500 and 600° with fuming nitric acid to insure complete decomposition when analyzing.

Bromopaeonol, $C_6H_2(OH)(OCH_3)(Br)(COCH_3)$.—To paeonol in 80% acetic acid one molecule of bromine was added. Upon stirring a few moments a white mass separated out.

Subst., 0.2586 g.; AgBr, 0.2000 g.
Calc. for $C_9H_9O_3Br$: Br, 32.7. Found: 32.9.

From alcohol long, white needles melting at 169° were obtained. This substance was found by Brull[1] as one of the products of bromination of paeonol acetate in carbon disulfide and was reported by him as having a melting point of 171°.

Bromopaeonol Phenylhydrazone, $C_6H_2(OH)(OCH_3)(Br)[C(NNHC_6H_5)CH_3]$.—Equal molecules of bromopaeonol and phenylhydrazine were refluxed in alcohol solution for half an hour. On cooling, especially after evaporation of part of the solvent, the product crystallized out.

Subst., 0.1883 g.; AgBr, 0.1065 g.
Calc. for $C_{15}H_{15}O_2N_2Br$: Br, 23.9. Found: 24.0.

From alcohol long, slender, yellow needles melting 172.5–173.5° were obtained. The substance was insoluble in boiling alkali.

Bromopaeonol *p*-Bromophenylhydrazone, $C_6H_2(OH)(OCH_3)(Br)[C(NNHC_6H_4Br)CH_3]$.—Made in a mixture of glacial acetic acid and alcohol. On cooling the compound crystallized out.

Subst., 0.2052 g.; 0.1646 g.; AgBr, 0.1852 g.; 0.1482 g.
Calc. for $C_{15}H_{14}O_2N_2Br_2$: Br, 38.64. Found: 38.37, 38.27.

From glacial acetic acid dull, yellow, monoclinic plates melting at 189.5° were obtained. The substance was insoluble in boiling alkali.

Bromopaeonol 2,4,6-Tribromophenylhydrazone, $C_6H_2(OH)(OCH_3)(Br)[C(NNHC_6H_2Br_3)CH_3]$.—Equal molecules of bromopaeonol and tribromophenylhydrazine were refluxed $^1/_2$ hour in a mixture of glacial acetic acid and alcohol. The compound separated on cooling.

Subst., 0.1748 g.; AgBr, 0.2276 g.
Calc. for $C_{15}H_{12}O_2N_2Br_4$: Br, 55.9. Found: 55.4.

From 80% acetic acid white needles melting at 169 to 171° were obtained. The substance was insoluble in boiling alkali. In analyzing this compound, it was necessary to heat between 500 and 600° with fuming nitric acid in order to get complete decomposition.

[1] *Ber.*, **30**, 301 (1897).

Bromopaeonol Methylether, $C_6H_2(OCH_3)_2(Br)(COCH_3)$.—Bromopaeonol was dissolved in a little over one molecule of a 5% solution of sodium hydroxide. One molecule of dimethyl sulfate was added and the two warmed to about 90°; the mixture was then thoroughly shaken. The reaction took place and a solid crystallized out. To make sure of complete methylation, another treatment with sodium hydroxide and dimethyl sulfate was made.

The substance may also be prepared by the action of one molecule of bromine in acetic acid on one molecule of paeonol methylether in dilute alcohol. The substance crystallized out.

Subst., 0.1656 g.; AgBr, 0.1213 g.
Calc. for $C_{10}H_{11}O_3Br$: Br, 30.9. Found: 31.1.

From dilute alcohol white needles melting at 139 to 140° were obtained. On treatment with phenyl hydrazine in the usual way no phenylhydrazone of this compound could be obtained nor of paeonol methylether.

ω-Tribromo-bromopaeonol, $C_6H_2(OH)(OCH_3)(Br)(COCBr_3)$. — Brull[1] reported that he obtained a mixture of dibromo- and tribromopaeonol by the action of bromine on bromopaeonol in glacial acetic acid. No results in this research were obtained by that method. By the action of bromine in the presence of a little iodine the above tribromo derivative was obtained. Two g. of perfectly dry bromopaeonol was treated with 3 to 3.5 g. of bromine to which a crystal of iodine had been added. An immediate evolution of hydrobromic acid took place and the mass turned to a liquid. This was allowed to stand 10 to 12 hours, at the end of which time no more hydrobromic acid was evolved and a solid cake remained. This was washed with water several times and then purified.

Subst., 0.2449 g., 0.2894 g.; AgBr, 0.3800 g.; 0.4485 g.
Calc. for $C_9H_6O_3Br_4$: Br, 66.4. Found: 65.9, 66.0.

From alcohol lemon yellow needles were obtained melting at 123 to 124°. To prove the constitution of this substance, it was reduced with 80% acetic acid and zinc dust for about an hour. On pouring into water pure bromopaeonol crystallized out. Upon treatment with two molecules of phenylhydrazine a dark yellow substance resulted which was difficult to purify. Analysis gave slightly low results for the splitting out of one molecule of water and two of hydrobromic acid and entrance of two phenylhydrazine residues, the product probably being $C_6H_2(OH)(OCH_3)(Br)[CC(NNHC_6H_5)_2Br]$.

Nitrobromopaeonol, $C_6H(OH)(OCH_3)(Br)(NO_2)(COCH_3)$.—A molecule of bromopaeonol, free from alcohol, was dissolved in 10 times its weight of glacial acetic acid, mixed with the same volume of nitric acid (sp. gr. 1.42) and allowed to stand 15 to 20 hours. The bromopaeonol gradually dissolved and the solution turned yellow. This was poured into water

[1] *Ber.*, **30**, 301 (1897).

and a precipitate gradually separated. The presence of any alcohol caused the original nitration to go too violently and no crystalline substance was obtained.

Subst., 0.1760 g.; AgBr, 0.1163 g.
Calc. for $C_9H_8O_5NBr$: Br, 27.7. Found: 28.1.

From absolute alcohol long, white, hairy needles melting at 112 to 114° were obtained.

Nitrobromopaeonol Phenylhydrazone, $C_6H(OH)(OCH_3)(Br)(NO_2)[C(NNHC_6H_5)CH_3]$.—The condensation was carried out in warm alcohol solution, the solid crystallizing on cooling. Care had to be taken not to have the alcohol boiling or to use excess of phenylhydrazine, otherwise poor results were obtained.

Subst., 0.2033 g.; AgBr, 0.0979 g.
Calc. for $C_{15}H_{14}O_4N_3Br$: Br, 21.0. Found: 20.8.

From alcohol or dilute acetic acid saffron-colored crystals melting at 204.5 to 205.5° were obtained. The substance was gradually soluble in cold, readily in warm alkali.

Nitropaeonol, $C_6H_2(OH)(OCH_3)(NO_2)(COCH_3)$.—One part of paeonol was dissolved in 6 parts of glacial acetic acid and to this was added 4 parts of nitric acid (sp. gr. 1.42). On standing for a few minutes at room temperature, a slight greenish tinge appeared in the solution which gradually became darker and darker colored until it was almost black. At this stage, the mixture had warmed up and nitrous fumes came off. The gas continued to be evolved for some time, then it stopped and the solution turned reddish with a simultaneous separation of crystals. In the course of an hour after this when the reaction was complete the crystals were filtered off and washed with alcohol.

Subst., 0.2086 g.; N, 11.9 cc.; 770 mm., 24.0°.
Calc. for $C_9H_9O_5N$: N, 6.6. Found: 6.7.

From alcohol white needles melting at 155° were obtained.

Nitropaeonol Phenylhydrazone, $C_6H_2(OH)(OCH_3)(NO_2)[C(NNHC_6H_5)CH_3]$.—Made in alcohol solution, the compound separated on cooling.

Subst., 0.1893 g.; N, 23.0 cc.; 772 mm., 22.5°.
Calc. for $C_{15}H_{15}O_4N_3$: N, 13.9. Found: 14.3.

From glacial acetic acid orange needles melting at 215.5 to 216.5° were obtained. The substance was slightly soluble in cold, readily in warm alkali.

Nitropaeonol Methylether, $C_6H_3(OCH_3)_2(NO_2)(COCH_3)$.—Nitropaeonol, dissolved in slightly over a molecule of cold 5% aqueous sodium hydroxide was treated with a molecule of dimethyl sulfate. The mixture was heated to about 100° and shaken thoroughly. On cooling, the compound crystallized out.

Subst., 0.1669 g.; N, 8.6 cc.; 758 mm., 22.5°.
Calc. for $C_{10}H_{11}O_5N$: N, 6.2. Found: 6.1.

From alcohol slender, white needles melting at 131° were obtained. On exposure to light, the crystals gradually turned yellow-red in color. By treatment of a boiling alcohol solution of one molecule of the nitropaeonol methylether with a boiling alcohol solution of one molecule of phenylhydrazine, an immediate precipitate resulted which from glacial acetic acid crystallized in orange needles melting at 215.5 to 216.5° and proved to be the phenylhydrazone of nitropaeonol.

The nitropaeonol methylether may also be made by the nitration of paeonol methylether following the directions for the nitration of paeonol but poor yields were obtained.

Aminopaeonol, $C_6H_2(OH)(OCH_3)(NH_2)(COCH_3)$.—Nitropaeonol was warmed with tin and hydrochloric acid until it went completely into solution. This solution was filtered, diluted and the tin precipitated by saturating hot with hydrogen sulfide. On filtration and evaporation, the hydrochloride of the aminopaeonol separated. During the evaporation, passage of hydrogen sulfide through the solution prevented decomposition. The hydrochloride was very soluble in water and crystallized out white on addition of conc. hydrochloric acid. It was dissolved in water and treated with sodium sulfite to neutralize the acid. The free amino compound separated out.

Subst., 0.3144 g.; N, 21.0 cc.; 764 mm., 20.5°.
Calc. for $C_9H_{10}O_3N$: N, 7.7. Found: 7.8.

From dilute alcohol greenish yellow monoclinic prisms melting at 112 to 113° were obtained.

The hydrochloride dissolved in a little water and treated with a concentrated solution of chloroplatinic acid yielded on standing a brown powder which was purified by washing with alcohol and ether. It was then dried in a desiccator and subsequently at 100° in an air bath. On analysis it proved to be the chloroplatinate.

Subst., 0.2936 g.; Pt, 0.0738 g.
Calc. for $(C_9H_{10}O_3N)H_2PtCl_6$: Pt, 25.25. Found: 25.13.

In an unsuccessful attempt to prove the structure of nitroresacetophenone and nitropaeonol the following derivatives of resacetophenone were prepared:

Nitration of Monoacetylresacetophenone, $C_6H_3(OH)^2(OCOCH_3)^4(COCH_3)^3$.—Acetylresacetophenone,[1] dissolved in glacial acetic acid and treated with nitric acid, yielded the same product as was obtained by the nitration of resacetophenone. A second sample of acetylresacetophenone, which had been standing several days, when treated the same way acted differently. After remaining overnight, a compound crystallized out.

[1] *J. prakt. Chem.*, [2] **23**, 147 (1881).

This proved to be dinitroacetylresacetophenone. Further experiments with nitration of acetylresacetophenone in a mixture of alcohol and glacial acetic acid, first in equal weights, then in varying proportions, gave sometimes the above substance melting at 121° and sometimes a mixture of this compound with another compound, dinitro-resacetophenone, melting at 166 to 167°. The two were separated by treating with warm alcohol, the former being readily soluble while the latter dissolved only in boiling alcohol. The indications were that increasing the amount of acetic acid tended to give more of the 166° substance.

Dinitroacetylresacetophenone, $C_6H(OH)^2(OCOCH_3)^4(NO_2)_2^{3.5}(COCH_3)^1$.—

Subst., 0.2290 g., 0.2176 g.; N, 18.6 cc.; 768 mm., 20.0°; 18.2 cc.; 751 mm., 20.0°.
Calc. for $C_{10}H_8O_8N_2$: N, 9.8. Found: 9.6, 9.6.

From absolute alcohol white plates melting 121 to 122° were obtained.

Dinitroresacetophenone, $C_6H(OH)_2^{2.4}(NO_2)_2^{3.5}(COCH_3)^1$.—

Subst., 0.1444 g.; N, 14.5 cc.; 762 mm., 22.0°.
Calc. for $C_8H_6O_7N_2$: N, 11.5. Found: 11.7.

From absolute alcohol very slightly yellowish crystals, resembling fine sand and melting 166 to 167° were obtained.

Dinitroresacetophenone Phenylhydrazone, $C_6H(OH)_2(NO_2)_2[C(NNHC_6H_5)CH_3]$.—The condensation was carried on in alcohol solution and the compound crystallized out.

Subst., 0.1674 g.; N, 24.2 cc.; 765 mm., 19.0°.
Calc. for $C_{14}H_{12}O_6N_4$: N, 16.8. Found: 17.0.

From glacial acid reddish brown crystals darkening at 238° and decomposing at 242.5° were obtained.

Acetaminoresacetophenone, $C_6H_2(OH)_2^{2.4}(NHCOCH_3)^5(COCH_3)^1$. — Resacetophenone[1] was nitrated, then reduced according to the directions of Nencki.[2] In reducing the nitro compound better results were obtained, if during the evaporation of the aminoresacetophenone hydrochloride a free flame was used and a stream of hydrogen sulfide was passed in continually. This hydrochloride was treated with excess of thioacetic acid and warmed on a water bath. The resulting mass was then boiled with a little water to destroy the excess acetic acid and remove any unchanged hydrochloride.

Subst., 0.2606 g.; N (moist), 15.3 cc.; 760 mm., 23.0°.
Calc. for $C_{10}H_{11}O_4N$: N, 6.5. Found: 6.6.

From water, white needles melting 254° were obtained.

Derivatives of Resodiacetophenone, $C_6H_2(OH)_2^{2.4}(COCH_3)_2^{1.5}$. Resodiacetophenone was synthesized by the method of Eijkmann.[3]

[1] *J. prakt. Chem.*, [2] **23**, 147 (1881).
[2] *Ibid.*, [2] **23**, 537 (1881).
[3] *Chem. Weekblad*, **1**, 453 (1904); *Chem. Centr.*, **1**, 1597 (1904).

Nitroresodiacetophenone, $C_6H(OH)_2^{2,4}(COCH_3)_2^{1,5}(NO_2)^3$. — Resodiacetophenone was placed in a flask immersed in salt and ice. Twelve parts of cold, fuming nitric acid were added and the mixture allowed to stand half an hour, then poured into water. The crude nitro compound separated. A better yield was obtained by dissolving one part of resodiacetophenone in 3 parts of glacial acetic acid, cooling to 0°, adding 5 parts of fuming nitric acid, allowing to stand a few minutes, then pouring into water.

Subst., 0.2879 g.; 0.2590 g.; N, 15.3 cc.; 763 mm., 20.0°; 14.0 cc.; 753 mm., 23.0°.
Calc. for $C_{10}H_8O_6N$: N, 5.8. Found: 6.2, 6.2.

From glacial acetic acid small, white needles melting at 231° were obtained. The proof of the structure of nitroresodiacetophenone was carried out as follows: one part of resodiacetophenone or nitroresodiacetophenone was added to 6 parts of fuming nitric acid. Violent action took place with evolution of nitrous fumes. When these had ceased, the mixture was heated for 5 to 10 minutes until no more fumes appeared. On cooling, crystals separated. They were drained, washed with a little glacial acetic acid to get rid of the excess nitric acid and crystallized from glacial acetic acid. The substance proved to be symmetrical trinitro resorcin or styphinic acid, the structure of which is known, thus showing the nitro group of nitroresodiacetophenone to be between the two hydroxyl groups.

Subst., 0.1911 g.; N, 27.8 cc.; 765 mm., 16.0°.
Calc. for $C_6H_3O_8N_3$: N, 17.1. Found: 17.3.

From glacial acetic acid white needles melting at 175° were obtained.

Nitroresodiacetophenone Monophenylhydrazone, $C_6H(OH)_2(COCH_3)[C(NNHC_6H_5)CH_3](NO_2)$.—A molecule of phenylhydrazine was added to a molecule of nitroresodiacetophenone dissolved in glacial acetic acid. After standing a half-hour in the cold, any crystals which had formed were filtered off and rejected and the filtrate poured into water.

Subst., 0.0950 g.; N, 10.4 cc.; 765 mm., 18.0°.
Calc. for $C_{16}H_{15}O_5N_3$: N, 12.7. Found: 12.9.

From dilute alcohol a light yellow powder darkening at 220° and decomposing sharply at 235° was obtained. The substance was soluble in cold alkali.

Nitroresodiacetophenone Diphenylhydrazone, $C_6H(OH)_2[C(NNHC_6H_5)CH_3]_2(NO_2)$.—The condensation was carried out by warming in glacial acetic acid two molecules of phenylhydrazine and one molecule of nitroresodiacetophenone. The compound separated out.

Subst., 0.1294 g.; N, 18.7 cc.; 761 mm., 22.0°.
Calc. for $C_{22}H_{21}O_4N_5$: N, 16.7. Found: 16.8.

From acetone massive, lemon-yellow needles were obtained which on standing in air or in a desiccator became darker until they were orange-red in color. If the crude substance was dissolved in acetone and precip-

itated with alcohol, the red form was obtained directly. If either form was heated to 100° for a few minutes, the color turned darker red and the color remained on cooling. The yellow compound obtained from acetone, dried quickly on a clay plate and then exposed to air lost weight gradually, indicating possibly acetone of crystallization. The compound was crystallized twice and then decomposed at 273°. It was dried six hours at 100° before analyzing. The substance was only slightly soluble in cold, readily in warm alkali.

Bromoresodiacetophenone, $C_6H(OH)_2^{2,4}(COCH_3)_2^{1,5}(Br)^3$.—By the action of free bromine on resodiacetophenone, Torrey[1] was unable to get a pure bromo derivative. It was prepared easily as follows: Resodiacetophenone was dissolved in cold glacial acetic acid and bromine vapors were gradually passed in or one molecule of bromine dissolved in glacial acetic was gradually added. The solution had to be kept cold or else the yield and purity of the product was materially diminished. A precipitate began to settle in the course of a few minutes.

Subst., 0.3813 g.; AgBr, 0.2640 g.
Calc. for $C_{10}H_9O_4Br$: Br, 29.3. Found: 29.4.

From glacial acetic acid white plates melting at 205° were obtained. From benzene, however, large, pointed, transparent crystals formed which evidently held benzene of crystallization for they effloresced in air to a white powder which melted at 205°.

The structure of the bromoresodiacetophenone was proven in a similar manner to the nitroresodiacetophenone. On treatment with fuming nitric acid or even less strong nitric acid, the bromoresodiacetophenone changed readily to symmetrical trinitroresorcin thus showing the bromine was replaced by a nitro group and therefore that the bromine must be between the two hydroxyl groups.

Derivatives of Salicyl Aldehyde, $C_6H_4(OH)(CHO)$.

Salicyl Aldehyde *o*-Tolylhydrazone, $C_6H_4(OH)(CHNNHC_6H_4CH_3)$.—The substance was made according to the directions of Auwers.[2] On long standing with cold alkali, a slight color developed but the compound did not dissolve until the alkali was hot.

Salicyl Aldehyde 2,4,6-Tribromophenylhydrazone, $C_6H_4(OH)(CHNNHC_6H_2Br_3)$.—Equal molecules of salicyl aldehyde and tribromophenylhydrazine were refluxed in alcohol for about an hour, then poured into water.

Subst., 0.2431 g.; AgBr, 0.3038 g.
Calc. for $C_{13}H_9ON_2Br_3$: Br, 53.4. Found: 53.2.

From dilute alcohol long, white needles melting at 100° were obtained. The compound was insoluble in hot, gradually soluble in boiling alkali with decomposition.

[1] THIS JOURNAL, 30, 858 (1908).
[2] *Ann.*, **365**, 320 (1909).

5-Nitrosalicyl Aldehyde Benzidine, $[C_6H_3(OH)(NO_2)(CH)]_2N_2(C_6H_4)_2$. —One molecule of benzidine and two of 5-nitrosalicyl aldehyde were warmed together in alcohol and a red crystalline mass separated.

Subst., 0.1979 g.; N, 20.2 cc.; 757.5 mm., 20.5°.
Calc. for $C_{26}H_{18}O_6N_4$: N, 11.6. Found: 11.8.

From nitrobenzene red crystals not melting under 275° were obtained. The substance dissolved partially in boiling alkali.

3-Nitrosalicyl Aldehyde Benzidine, $[C_6H_3(OH)(NO_2)(CH)]_2N_2(C_6H_4)_2$. —The substance was made in the same way as the preceding compound.

Subst., 0.1818 g.; N, 18.3 cc.; 758 mm., 17.5°.
Calc. for $C_{26}H_{18}O_6N_4$: N, 11.6. Found: 11.8.

From nitrobenzene bright red crystals were obtained not melting under 275°. The substance dissolved somewhat in boiling alkali and was slightly more soluble than the 5-nitro derivative.

Derivatives of *p*-Homosalicyl Aldehyde,[1] $C_6H_3(CH_3)^1(OH)^4(CHO)^5$.

***P*-Homosalicyl Aldehyde Phenylhydrazone,** $C_6H_3(CH_3)(OH)(CHNNHC_6H_5)$.—The substance was prepared as described in the literature.[2] It was soluble in warm to hot alkali.

***P*-Homosalicyl Aldehyde Hydrazone,** $C_6H_3(CH_3)(OH)(CHNNH_2)$.—*P*-Homosalicyl aldehyde was dissolved in a small amount of alcohol and poured into a water solution of a slight excess over one molecule of hydrazine hydrate. After standing for 5 minutes, water was added gradually until precipitation was complete.

Subst., 0.1426 g.; N, 22.0 cc.; 761 mm., 18.0°.
Calc. for $C_8H_{10}ON_2$: N, 18.0. Found: 18.2.

A white powder melting at 72 to 74° was obtained.

The compound was extremely difficult to crystallize so that the analysis was made on a crude sample. The substance was soluble in cold alkali.

Monobromo-*p*-homosalicyl Aldehyde, $C_6H_2(CH_3)(OH)(CHO)(Br)$.—A molecule of bromine was added to a glacial acetic acid solution (10 parts) of *p*-homosalicyl aldehyde (1 part). The mixture after standing an hour was poured into water.

Subst., 0.1396 g.; AgBr, 0.1236 g.
Calc. for $C_8H_7O_2Br$: Br, 37.2. Found: 37.7.

From dilute alcohol yellow crystals shrinking at 63° and melting at 65° were obtained.

Monobromo-*p*-homosalicyl Aldehyde Phenylhydrazone, $C_6H_2(CH_3)(OH)(Br)(CHNNHC_6H_5)$.—The substance was prepared in alcohol solution and precipitated by pouring into water.

Subst., 0.1327 g.; N, 10.6 cc.; 765 mm., 15.0°.
Calc. for $C_{14}H_{13}ON_2Br$: N, 9.2. Found: 9.5.

[1] *Ber.*, **11**, 773 (1878).
[2] *Ibid.*, **35**, 4105 (1902).

From 50% alcohol dirty yellow crystals melting at 140 to 141° were obtained. The substance was soluble in warm to hot alkali.

Derivatives of 5-Methyl-2-hydroxybenzophenone, $C_6H_3(OH)^1(CO\text{-}C_6H_5)^2(CH_3)^5$.

The substance was prepared from *p*-cresol methylether, benzoyl chloride and aluminum chloride.[1]

5-Methyl-2-hydroxybenzophenone Azine, $[C_6H_3(OH)^1(CH_3)^5(CC_6\text{-}H_5)^2]_2N_2$.—Two molecules of the ketone dissolved in a little alcohol and one molecule of hydrazine sulfate in water were mixed and to them was added a little warm hydroxide solution. The whole was then refluxed from 8 to 10 hours, when crystals separated.

Subst., 0.1520 g.; N, 9.1 cc.; 763 mm., 18.0°.
Calc. for $C_{28}H_{24}O_2N_2$: N, 6.7. Found: 7.0.

From glacial acetic acid lemon yellow crystals melting at 259 to 260° were obtained. The substance is insoluble in boiling sodium hydroxide.

Hydrolysis Experiments.

A 10% solution of hydrochloric acid was used in these experiments. About 0.1 g. of substance was added to about 50 cc. of acid and boiled under a reflux condenser. The substances were all insoluble but on hydrolyzing decomposed and the products went into solution.

	Hydrolysis.
1. Salicyl aldehyde *o*-tolylhydrazone	15 minutes, complete
2. Salicyl aldehyde *p*-bromophenylhydrazone	30 minutes, partial
3. *p*-Homosalicyl aldehyde phenylhydrazone	15 minutes, complete
4. *p*-Homosalicyl aldehyde *p*-bromophenylhydrazone	60 minutes, partial
5. Paeonol phenylhydrazone	30 minutes, complete

A few drops of alcohol were added to a set of the above mixtures and heated. 1, 3 and 5 were completely hydrolyzed in about 10 minutes and 2 and 4 in about half an hour.

Sodium Salts.

Paeonol and bromoacetonaphthol were dissolved in a few cc. of absolute alcohol and to them was added one atom of sodium dissolved in absolute alcohol. On evaporation to dryness in a vacuum desiccator sodium salts were obtained. They were ground to a powder and the following tests were made:

	Sodium salt of paeonol phenylhydrazone.	Sodium salt of bromoacetonaphthol phenylhydrazone.
Cold water	complete hydrolysis	complete hydrolysis
Hot water	complete hydrolysis	complete hydrolysis
1% cold sodium hydroxide	complete hydrolysis	complete hydrolysis
1% hot sodium hydroxide	partial solution	complete hydrolysis
10% cold sodium hydroxide	complete hydrolysis	complete hydrolysis
10% hot sodium hydroxide	complete solution	complete hydrolysis
Cold alcohol	complete solution	complete solution
Hot alcohol	complete solution	complete solution

[1] *Ber.*, 36, 3892 (1903).

Summary.

1. A thorough study of various phenylhydrazones of *o*-hydroxyaldehydes and ketones indicates that the introduction of any atom or group of atoms into any part of the molecule causes the solubility in 10% aqueous alkali to decrease.

2. Five different explanations for this alkali insolubility are briefly discussed and shown to be out of the question. A sixth explanation suggested by Torrey, namely, tautomerism between phenol and quinoid form is taken up in detail and from new experimental data the improbability of it is also shown.

3. A simple explanation is offered and it is shown to agree with all the experimental facts. The insolubility is due to the great tendency of the sodium salts of these phenols to hydrolyze, coupled with the fact that the free phenols are extremely insoluble in water.

4. A brief discussion is given of the various nitrophenol derivatives, many of which cause the molecule to increase in solubility in alkali instead of decrease as might be expected. This is probably due to the formation of the aci-nitro compounds which are much stronger acids than the phenols themselves.

[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY, BUREAU OF PLANT INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THE PREPARATION OF METOL (*N*-METHYL-*p*-AMIDOPHENOL SULFATE).

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In 1890 Andresen[1] obtained a German patent for the application as photographic developers of *p*-amidophenol, *p*-amidocresol and the "substituted compounds of *p*-amidophenol and *p*-amidocresol." In the following year Hauff[2] secured patents in Germany and England for the use as photographic developers of *N*-alkylated derivatives of amidophenols, amidocresols, amidoxylenols, and aromatic diamines, the German patent stating that it is dependent upon the patent of Andresen "insofar as it is concerned with the derivatives of the *p*-amidophenols." In the specifications for Hauff's patent he gives directions for making up a developing solution using "methyl-*p*-amido-*m*-cresol (Metol)." This appears to be the first use of the word "Metol," which word Hauff later registered as a trade-mark in Germany,[3] England,[4] and the United States.[5] Paul,[6]

[1] D. R. P. 60174.

[2] D. R. P. 69582, E. P. 15434.

[3] German Waarenzeichen No. 21540 (1897).

[4] English trade-mark No. 170477 (1893), English trade-mark No. 222388 (1899).

[5] U. S. trade-mark No. 57145 (1906).

[6] *Z. angew. Chem.*, 10, 171–4 (1897).