The changes are even more erratic and irregular in the halogen addition products. An extreme case is found in the *o*-tolyl selenide dichloride and dibromide melting at 152° and 84°, respectively. The halogen substitution products, thus far reported, exhibit differences which are more nearly constant than is observed among the halogen addition products.

CHEMICAL LABORATORIES,
INDIANA UNIVERSITY, BLOOMINGTON, IND.,
March, 1908.

(CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.)

HYDRAZONES OF AROMATIC HYDROXYKETONES, ALKALI-INSOLUBLE PHENOLS.

SECOND PAPER.

BY HENRY A. TORREY AND H. B. KIPPER.

Received March 13, 1908.

Although it is a very general rule, so general indeed that it is almost universal, that phenols are soluble in aqueous alkalies, there are certain substances of this class that are marked exceptions. The work described in this paper consists of an extension of the list of such compounds, and some investigation of the conditions to which this alkali-insolubility is due. While studying the phenylhydrazones of certain hydroxy aceto- and benzophenones, it was found, as mentioned in an earlier paper,[1] that when the free hydroxyl was in the ortho position with reference to the substituted ketone group, the substance was insoluble in strong aqueous alkalies. Substances showing this characteristic property have been obtained and studied by others. O. Anselmino[2] studied the phenylhydrazones of homosalicylaldehydes and obtained alkali-insoluble compounds similar to ours. Liebermann[3] first discussed in detail the alkaline insolubility of benzene azonaphthol, which was later studied by Goldschmidt and R. Brubacher,[4] McPherson[5] and Hantzsch and Farmer.[6] St. v. Kostanecki has obtained certain nitrogen-free phenols which are insoluble in alkalies; thus A. Cornelson and St. v. Kostanecki[7] report that 2-hydroxy-benzaldiacetophenone,

$$HOC_6H_4CH(CH_2COC_6H_5)_2,$$

is insoluble in warm dilute sodium hydroxide, although it does dissolve in hot 15 per cent. potassium hydroxide, and St. v. Kostanecki and R. v. Salis[8] state that 2-ethoxybenzalresacetophenonmonoethyl ether,

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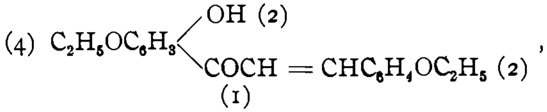
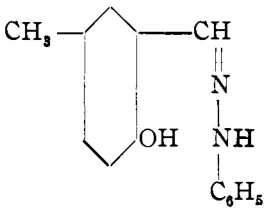
[1] THIS JOURNAL, 29, 77.
[2] *Ber.*, 35, 4099.
[3] *Ibid.*, 16, 2858.
[4] *Ibid.*, 24, 2306.
[5] *Ibid.*, 28, 2418.
[6] *Ibid.*, 32, 3100.
[7] *Ibid.*, 29, 242.
[8] *Ibid.*, 32, 1030.



$$(4)\ C_2H_5OC_6H_3\begin{cases} OH\ (2) \\ \underset{(1)}{COCH} = CHC_6H_4OC_2H_5\ (2) \end{cases},$$

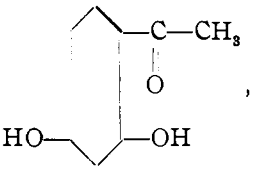
is insoluble in aqueous alkalies. Rogow[1] and R. Fosse and A. Robyn,[2] by the condensation of hydroxyaldehydes with β-naphthol, obtained dinaphthoxanthenes, containing hydroxyl groups, which were insoluble in aqueous sodium hydroxide. Rogow[1] mentions also condensation products of hydroxy-aldehydes with β-naphthylamine which are almost insoluble in dilute alkalies. The phenylhydrazone of *p*-homosalicylaldehyde, as obtained by Anselmino, is a compound entirely insoluble in cold, highly concentrated alkalies. The phenylhydrazone of salicylaldehyde, on the other hand, although its hydroxyl group is in the ortho position to the side chain carrying the hydrazone radical, is, nevertheless, soluble in alkalies. The solubility of the phenol is therefore influenced by the presence of the methyl group, and this effect is even more marked when more than one methyl group is present. Anselmino prepared a number of derivatives of this nature, including in addition to the phenylhydrazones, azines and semicarbazones. Those phenoxyaldehydes, however, which gave phenylhydrazones, insoluble in aqueous sodium hydroxide, gave azines and semicarbazones which were soluble in this reagent. He found also that phenylhydrazones of all *para*-hydroxyaldehydes were normally reacting phenols, dissolving easily in alkalies of all concentrations, and being reprecipitated with acids. Our investigation of the phenylhydrazones of the *o*-hydroxy-, aceto- and benzophenones was begun with the idea of obtaining a product of a secondary condensation between the hydroxyl group and the imide group, and the alkali-insolubility of many of the phenylhydrazones which we obtained lent color to the belief that such a condensation had actually occurred. The analytical results and the subsequent work, however, made such a conclusion untenable. We have already mentioned the influence of the methyl groups on the alkali-insolubility of the derivatives of the aldehydes, as studied by Anselmino; in none of the compounds which we have investigated is there an alkyl group directly attached to the ring, but we have found that the presence of other groups in the ring has the same



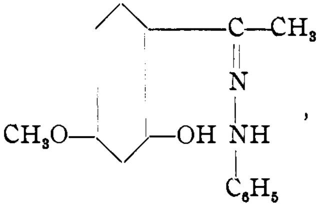
[1] *Ber.*, **33**, 3535; *J. pr. Ch.* [2], **72**, 320.

[2] *Compt. rend.*, **132**, 789; **137**, 858; **138**, 2820; **140**, 1538.

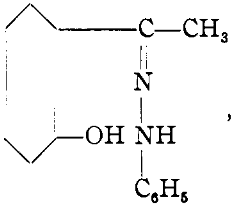
influence. Our work has been directed chiefly toward the study of phenylhydrazones and other similar derivatives of resacetophenone and resodiacetophenone. In resacetophenone,



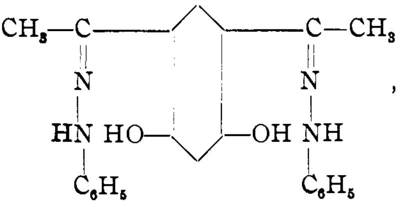
one hydroxyl group is ortho and the other para to the ketone side chain and its phenylhydrazone is, as would be expected, easily soluble in alkalies. The phenylhydrazone of paeonol,



however, in which the only free hydroxyl is ortho to the large side chain, is insoluble in aqueous alkalies, although paeonol itself is readily soluble. Since the phenylhydrazone of *o*-hydroxyacetophenone,



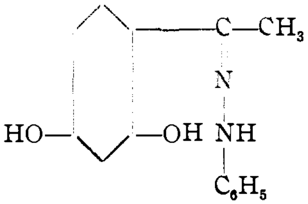
is soluble in alkalies, it is evident that the methoxy group in paeonol has a real influence upon the solubility. We have found also that the $C_6H_5COO—$, the $CH_3C=NNHC_6H_5$, and the $C_6H_5C=N.NHC_6H_5$ groups are contributing factors in this phenomenon of alkaline insolubility. To make clearer the influence of these last two groups upon the solubility, it is only necessary to call to notice the fact that although the phenylhydrazone of *o*-hydroxyacetophenone, whose formula has just been given, is soluble, the bisphenylhydrazone of resodiacetophenone,



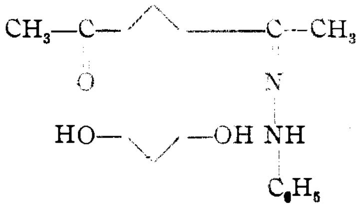
is exceedingly insoluble, even in hot aqueous alkalies. Thus, if we consider the influence of the substituting groups upon one hydroxyl at a time, we may say that the insolubility is brought about by the joint influence of the $CH_3\overset{|}{C}=N—NHC_6H_5$ adjacent to the given hydroxyl and of the other $CH_3\overset{|}{C}=N—NHC_6H_5$, this second group playing the part of the methoxy group in paeonol or the methyl groups in the aldehyde derivatives. While the benzidine derivative of resodiacetophenone, in which two molecules of benzidine have condensed with two molecules of the ketone, shows the same insolubility toward alkalies as the phenylhydrazone, the azine and semicarbazones are soluble. If we tabulate the phenols that we have studied according to their solubility in aqueous alkalies, they fall into the following groups:

Soluble in Aqueous Alkalies.

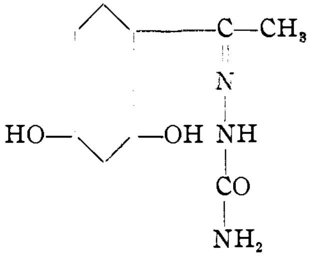
Phenylhydrazone of resacetophenone,



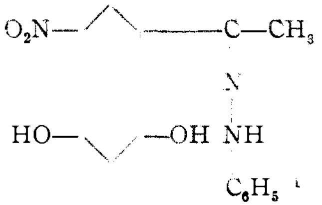
Monophenylhydrazone of resodiacetophenone,



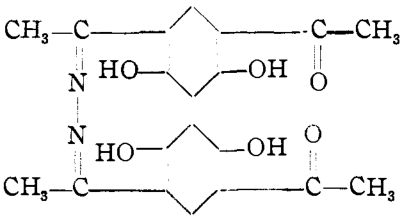
Semicarbazone of resacetophenone,



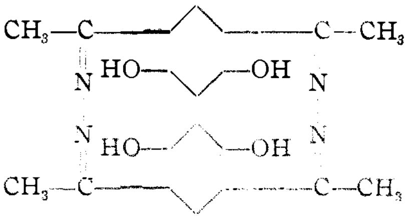
Phenylhydrazone of nitroresacetophenone,



Monoazine derivative of resodiacetophenone.



Bisazine derivative of resodiacetophenone.



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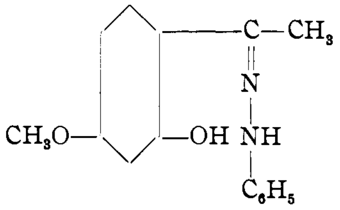
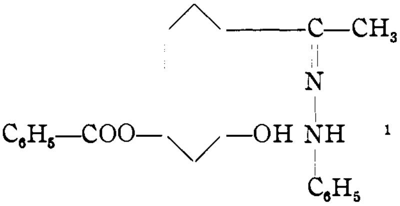
[1] Position of nitro group not proved.

Insoluble in Aqueous Alkalies.

Phenylhydrazone of paeonol,

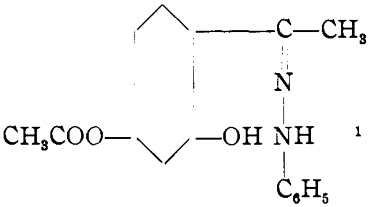


Phenylhydrazone of resacetophenone-4-monobenzoate,



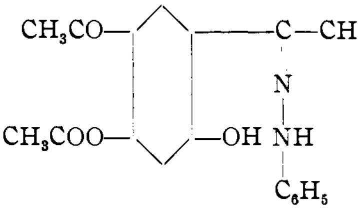
[1]

Phenylhydrazone of resacetophenone-4-monoacetate,



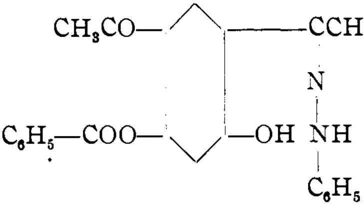
[1]

Phenylhydrazone of resodiacetophenone monacetate,



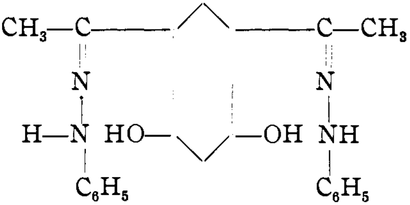
[2]

Phenylhydrazone of resodiacetophenone monobenzoate,

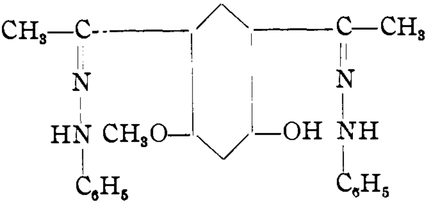


[2]

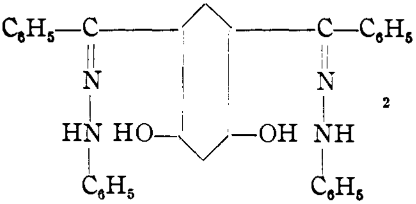
Bisphenylhydrazone of resodiacetophenone,



Bisphenylhydrazone of monomethyl ether of resodiacetophenone,



Bisphenylhydrazone of dibenzoresorcinol,



[2]

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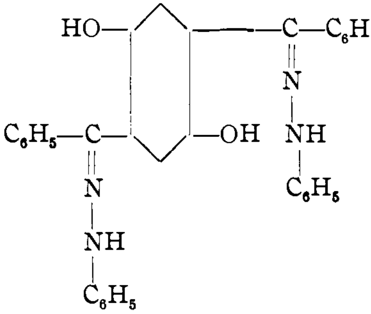
[1] Position of Br not proved.

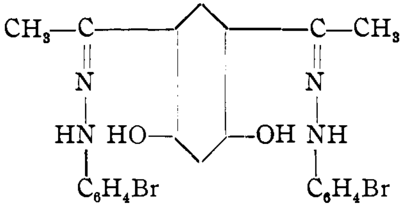
[2] Saponified by alkalies.

Bisphenylhydrazone of dibenzohydroquinonol,

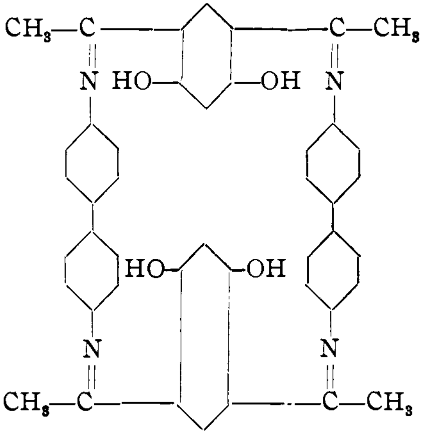


[1]

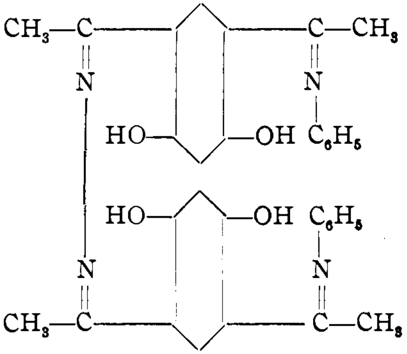
Bis *p*-bromphenylhydrazone of resodiacetophenone,



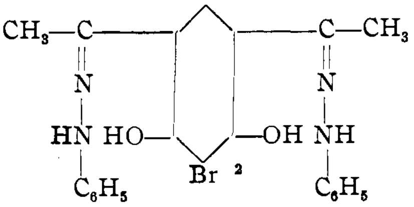
Condensation product of benzidine and resodiacetophenone,



Dianilido monazine derivative of resodiacetophenone,



Bisphenylhydrazone of monobromresodiacetophenone,



[2]

It will be noticed that in the compounds that we have studied, the insolubility in aqueous alkalies is determined by the *two* following conditions: (1) The free hydroxyl group is ortho to a large side chain, as

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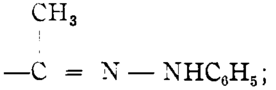
[1] THIS JOURNAL, 29, 81.

[2] Position of Br not proved.

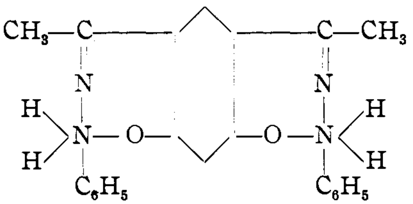


$$\overset{\displaystyle CH_3}{\underset{|}{}}\!\!\!\!-C = N - NHC_6H_5;$$

(2) other substituting groups are present, as OCH_3 or $OOCC_6H_5$, etc. If the basic group substituting the ketone oxygen is small, as in the bisazine or resodiacetophenone, the compound is soluble. Although Anselmino found that the phenylhydrazone of homosalicylaldehyde was insoluble in alkalies, K. Auwers and R. Bondy[1] have found that the phenylhydrazone of 5-nitro-2-hydroxy-1-methyl-3-benzaldehyde is soluble, while the same derivative of 5-nitro-4-hydroxy-1-methyl-3-benzaldehyde dissolves with difficulty, although we prepared phenylhydrazones from nitrated paeonol and from methylated nitroresoacetophenone. We have omitted them from the experimental part of this paper, as they have not as yet been sufficiently studied. The introduction of a less negative group, as bromine, into the ring, does not affect the solubility, for we found the bisphenylhydrazone of bromresodiacetophenone to be insoluble in alkalies.

It is, in our opinion, impossible to give at the present time an adequate explanation of the alkali-insolubility of these compounds.

Anselmino, in discussing the insoluble aldehyde derivatives, shows that no secondary condensation between the imide and hydroxyl group has taken place and calls attention to the fact that E. Fischer[2] has shown to be erroneous the statement of Causse[3] that such a condensation occurs between salicylaldehyde and phenylhydrazine in the presence of acetic anhydride. Not only do our analytical results show that in the phenylhydrazones recorded by us no such secondary condensation has occurred, but it is evident that no condensation of the kind could take place in the alkali-insoluble aniline and benzidine derivatives. This hypothesis is thus made untenable. A second hypothesis is that an inner salt has been formed, which, with the bisphenylhydrazone of resodiacetophenone, would be formulated as follows:



The comparatively weak acid nature of resodiacetophenone and the ortho hydroxy ketones studied makes such a hypothesis seem extremely

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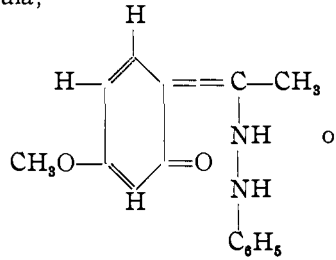
[1] *Ber.*, **37**, 3915.

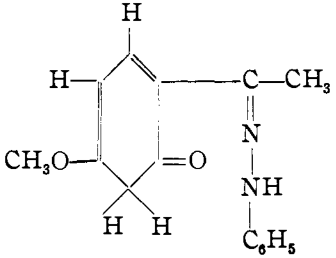
[2] *Ibid.*, **30**, 1240.

[3] *Compt. rend.*, **124**, 505.

unlikely, and further, it would offer no explanation for the difference in solubility in alkalies between the phenylhydrazone of *o*-hyroxyacetophenone and the phenylhydrazone of paeonol, or especially between the phenylhydrazone of salicylaldehyde and that of homosalicylaldehyde. In order to give some test to this theory, we have introduced a bromine atom into each of the phenylhydrazone groups in the bisphenylhydrazone of resodiacetophenone, thereby increasing the negativity of these groups and consequently decreasing the tendency toward salt formation, but without effect upon the solubility. It might be suggested that the insolubility is due simply to the fact that the acid nature of the phenol has been highly depressed by the introduction of basic groups, such as the phenylhydrazone or benzidine groups. If this were the true explanation, we should expect the phenylhydrazones of paeonol, or of the acetates or benzoates of resacetophenone and resodiacetophenone to be more soluble in alkalies than the phenylhydrazones of *o*-hydroxyacetophenone or of salicylaldehyde instead of less soluble. The alkali-insolubility of the compounds, then, cannot be explained by the hydrolytic action of water, especially when one considers that the bisphenylhydrazone of resodiacetophenone is not dissolved by a solution of sodium hydroxide of as great strength as 1 : 1. It was suggested in a former paper[1] that these compounds may have a quinoid structure and that the insolubility is due to this; thus for paeonol phenylhydrazone we have the formula,



or perhaps



We have been unable, however, to get any indication of such quinoid oxygen by the action of hydroxylamine, although it should be said that even if such a quinoid oxygen were present, it would be unlikely to react with hydroxylamine, and Anselmino[2] has shown that in the phenylhydrazones of the homosalicylaldehydes which are insoluble in aqueous alkalies, the phenylhydrazone group reacts with pyruvic acid to give its hydrazone, and that the phenol oxygen can be benzoylated by benzoyl chloride in pyridine solution. We are not, however, yet ready to entirely abandon the quinoid formulas as a possibility. The alkali-insoluble phenols that we have studied bear a certain analogy to 2-naphthol-1-

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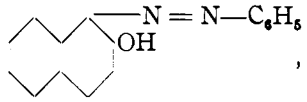
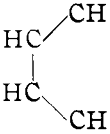
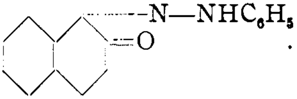
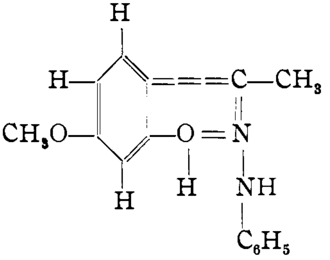
[1] This Journal, 29, 77.

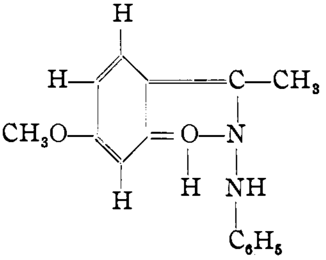
[2] *Ber.*, 35, 4101.

azobenzene, , which is insoluble in aqueous alkalies, and in which the four carbon chain  has the same influence on the solubility as the carbon-containing groups in our compounds. A. Goldschmidt and R. Brubacher,[1] by a study of the reduction products of its acetyl and benzoyl derivatives, have shown that in all probability this substance actually has this quinoid structure .

Fosse and Robyn[2] attribute the alkali-insolubility of the rather different compounds studied by them to the presence of a quadrivalent oxygen atom. If we assume that in our compounds, the oxygen of the hydroxyl is quadrivalent, the formula for the phenyl hydrazone of paeonol, for instance, might be written thus:



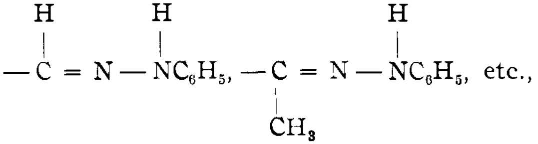
or



Since, however, quadrivalent oxygen ordinarily shows basic properties, such constitutions as these seem unlikely.

A very striking fact regarding the alkali-insoluble phenols is that although they are insoluble in aqueous alkalies they all dissolve with great ease in *alcoholic* alkalies and may be precipitated by mineral acids from these solutions unchanged.

In general, one may say regarding the alkali-insolubility of the phenols, that it is due to the combined influence of a large group as



$$-\overset{\overset{\displaystyle H}{|}}{C}=N-\overset{\overset{\displaystyle H}{|}}{N}C_6H_5,\ -\underset{\underset{\displaystyle CH_3}{|}}{C}=N-\overset{\overset{\displaystyle H}{|}}{N}C_6H_5,\ \text{etc.,}$$

in the ortho position to the hydroxyl and a carbon-containing group else-

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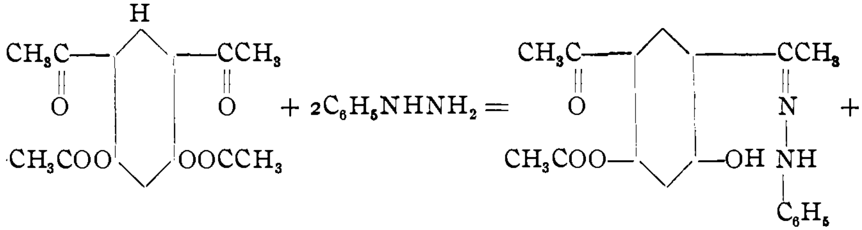
[1] *Ber.*, **24**, 2306.

[2] *Loc. cit.*

where in the ring. Whether the insolubility is due to an actual change in structure cannot at present be stated.

In the course of this work we have noticed some interesting cases of so-called steric hindrance, particularly in connection with the action of phenylhydrazine on resodiacetophenone diacetate and dibenzoate. When two molecules of phenylhydrazine were allowed to act on one molecule of resodiacetophenone diacetate in a hot alcoholic solution, containing acetic acid, the product obtained was the monophenylhydrazone of resodiacetophenone monoacetate, instead of the bisphenylhydrazone of the diacetate. The reaction proceeded, then, according to the following equation:



$CH_3CONHNHC_6H_5 + H_2O$.

The acetylphenylhydrazine formed in the reaction was isolated from the mother liquor. If a large excess of phenylhydrazine, not less than four molecules, for example, was allowed to act on the diacetate under the same conditions, both acetyl groups were eliminated with the formation of resodiacetophenone bisphenylhydrazone. The action of phenylhydrazine on the dibenzoate of resodiacetophenone is exactly analogous to its action on the diacetate. In an earlier paper[1] we stated that phenylhydrazine, acting upon resacetophenone dibenzoate gave the phenylhydrazone of the dibenzoate, melting at 183°. We have found, however, that this is erroneous, and that here also the benzoyl group adjacent to the keto side chain is eliminated, giving the phenylhydrazone of resacetophenonemonobenzoate. We experienced great difficulty in the determination of carbon in this compound, the results being generally about two per cent. high, until the method described in the experimental part of the paper was adopted. A more convenient way to prepare the same compound is to introduce the benzoyl group into resacetophenone phenylhydrazone, by means of the Schotten-Baumann reaction. Even though more than two molecules of benzoyl chloride were used, only one benzoyl group was introduced, since the hydroxyl group adjacent to the large side chain was protected from the action of the reagent.

Somewhat similar interference phenomena were noticed in attempting to prepare the bisphenylhydrazone of resodiacetophenonedimethyl ether.

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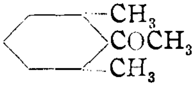
[1] THIS JOURNAL, 29, 80.

When the proper amount of phenylhydrazine was allowed to stand with the dimethyl ether in hot or cold alcohol or alcohol and acetic acid, only the unchanged resodiacetophenonedimethyl ether was obtained after crystallization from dilute alcohol. Other examples of hindrance of this kind are not wanting; for instance, Baum[1] and v. Meyer[2] have found that ketonic compounds of the type  do not react with the phenylhydrazine, and Klinger and W. Kolvenbach[3] were unable to obtain a phenylhydrazone from acetohydroquinone, although its dibenzoate gave a phenylhydrazone. On the other hand, we obtained the bisphenylhydrazone from the monomethyl ether of resodiacetophenone and from dibenzohydroquinone and dibenzoresorcinol.[4] In attempting to methylate the hydroxyl groups in the bisphenylhydrazone of resodiacetophenone, by acting upon its solution in alcoholic potash with methyl iodide, merely the unchanged hydrazone or its saponification products were obtained. Anselmino also found it impossible to methylate the phenylhydrazones of the homosalicylaldehydes.

In the latter part of this paper we describe the action of metanitrobenzoyl chloride upon hydroquinone diacetate and resorcinol diacetate in the presence of condensing agents such as anhydrous aluminium chloride, but we were entirely unsuccessful in our attempt to introduce the nitrobenzoyl group into the ring itself, in every case either one or both of the acetyl groups being replaced by the nitrobenzoyl group. Thus, from resorcinol diacetate, $C_6H_4(OOCCH_3)_2$, resorcinol *m*-nitrodibenzoate, $C_6H_4(OOCC_6H_4NO_2)_2$, was obtained. This replacement may be due, in part at least, to the greater volatility of acetyl chloride as compared with nitrobenzoyl chloride, and might be compared to the action of sulphuric acid on sodium chloride. Other analogous organic metathetical reactions have been observed, as for instance, the displacement of the acetyl group in acetaniline by the action of benzoyl chloride,[5] the formation of ethyl acetate by heating amyl acetate with ethyl alcohol at 240°, and of amyl benzoate by heating ethylbenzoate with amyl alcohol,[6] similar replacements by means of alcoholates,[7] the displacement of the methyl group[8] by the action of acetyl chloride and aluminium chloride

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[1] *Ber.*, 28, 3207.

[2] *Ibid.*, 29, 835.

[3] *Ibid.*, 31, 1216.

[4] THIS JOURNAL, **29**, 81.

[5] Paal and Otten, *Ber.*, **23**, 2587; and Ame Pictet, *Ibid.*, **23**, 3011.

[6] Friedel and Crafts, *Ann.*, **133**, 208.

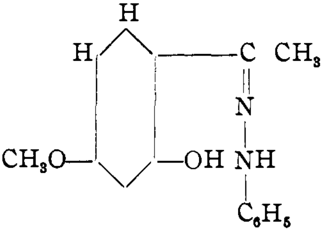
[7] J. Purdie, *Ber.*, **20**, 1554. Gattermann and Ritschke, *Ibid.*, **23**, 1738. Jackson and Torrey, *Am. Chem. J.*, 20, 404.

[8] Claus and Huth, *J. pr. Ch.* [2], **53**, 59.

and the replacement of the isobutyryl[1] by the acetyl group, and especially the formation of phenyl benzoate from phenyl acetate by the action of benzoyl chloride in the presence of zinc chloride.[3]

Experimental Part.

4-Monomethyl Ether of Resacetophenone Phenylhydrazone.—On shaking a molecule of resacetophenone phenylhydrazone[3] with slightly more than one molecule of dimethylsulphate in alkaline solution for eight hours, a compound was obtained which melted at 108° and was insoluble in ammonia and aqueous alkalies. Analysis showed that it was the monomethyl ether of resacetophenone phenylhydrazone; and since it is identical with the phenylhydrazone of paeonol, the methoxy group must be in the para position to the side chain:



It is soluble in alcohol, benzene, ether, chloroform, acetic acid, and alcoholic sodium or potassium hydroxide. It was purified by crystallization from dilute alcohol.

Calculated for $C_{15}H_{16}O_2N_2$: C, 70.31; H, 6.25.
Found: C, 70.03; H, 6.34.

Paeonol,[4] an aromatic ether, occurring in the root-bark of *Paeonia Moutan*, has been used for medicinal purposes in Japan and China since the earliest times. W. Nagai[5] showed that it was the 4-monomethyl ether of resacetophenone and Tahara[6] synthesized it from resacetophenone and found that the hydroxyl group ortho to the aceto group was methylated with some difficulty. In order to compare the product of the methylation of the phenylhydrazone of resacetophenone with the phenylhydrazine obtained from paeonol itself, the latter compound was prepared by allowing one molecule of resacetophenone, dissolved in dilute alkali, to stand for several days with one molecule of dimethyl sulphate. By using a shaking machine, the results were much more rapid and satisfactory. After acidifying, the paeonol was extracted with benzene, in which it is much more soluble than is resacetophenone. After evaporation of the solvent, the paeonol was purified by distillation *in vacuo*;

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[1] Brauchbar and Kohn, *Monatsh.*, 19, 27.

[2] Döbner, *Ann.*, 210, 255.

[3] *Bull. Soc. Chem.* [3], 6, 154.

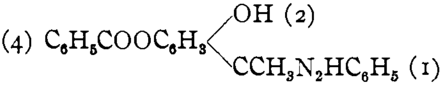
[4] *Ber.*, 25, 1292.

[5] *Ibid.*, 24, 2847.

[6] *Ibid.*, 24, 2460.

under 30 mm. the paeonol came over at about 210° and under 5 mm. at 180°. The crystals which formed on cooling melted at 50–51°. The phenylhydrazone of paeonol has already been described by F. Tiemann,[1] but was prepared by us for the sake of comparison and, as has been said, was identical with the monomethylether of resacetophenone phenylhydrazone described above.

The Phenylhydrazone of Resacetophenonemonobenzoate,



$$(4)\ C_6H_5COOC_6H_3\left\langle\begin{matrix}OH\ (2)\\ CCH_3N_2HC_6H_5\ (1)\end{matrix}\right.$$

.—By allowing the alkaline solution of the phenylhydrazone of resacetophenone to stand for several days at room temperature with more than two molecules of benzoyl chloride, a compound was obtained which was insoluble in cold aqueous alkalies, although solution with accompanying saponification takes place slowly. The insoluble precipitate was collected upon a filter, dried with suction and upon a clay plate. The benzoate was crystallized from hot alcohol, there being a considerable difference between the solvent powers of the hot and the cold solvent. M. p. 181–2°. It is also soluble in benzene and glacial acetic acid; in aqueous sodium hydroxide it is insoluble, but dissolves slowly on boiling. This compound was described in an earlier paper[2] as the phenylhydrazone of resacetophenone dibenzoate, since the analytical results pointed to this formula, but our subsequent work upon it has shown it to be the monobenzoate. Great difficulty was experienced in the combustion of this substance, the results for carbon usually being too high for the monobenzoate. Satisfactory results were finally obtained by proceeding as follows: The substance was mixed with fine copper oxide, and two reduced copper spirals were placed in the front part of the combustion tube. Before beginning the burning, a tube containing a reduced copper spiral was attached to the forward end of the combustion tube and dry air, free from carbon dioxide, was passed over this hot spiral, until the combustion tube proper was filled with an atmosphere rich in nitrogen and containing little oxygen. The special tube containing the copper spiral was then replaced by the absorption apparatus and the combustion was begun. The substance was heated very gradually and, as the burning progressed, oxygen was introduced into the tube. In two determinations a little oxygen was introduced into the rear end of the tube early in the combustion.

Calculated for $C_{21}H_{18}O_3N_2$: C, 72.83; H, 5.20; N, 8.09.
Found: C, 74.77, 73.96, 72.53, 72.92, 72.38, 72.75; H, 4.91, 6.08, 3.85, 6.15, 4.43, 5.41; N, 8.56, 7.84, 8.25, 7.99.

This same compound was also obtained from the resacetophenone diben-

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[1] *Ber.*, **24**, 2854.

[2] THIS JOURNAL, **29**, 80.

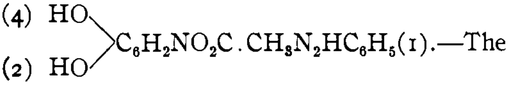
zoate[1] by the action of phenylhydrazine in hot alcoholic solution, which shows that the benzoyl group has replaced the hydrogen of one of the hydroxyl groups and not that of the imido group. The removal of one benzoyl group is in accord with our observations on the action of phenylhydrazine on resodiacetophenone diacetate and dibenzoate, described below, and it is reasonably certain that the benzoyl group removed is that nearest the ketone side chain.

The Phenylhydrazone of Resacetophenonemonoacetate.—One molecule of resacetophenonemonoacetate,[2] treated with slightly more than one molecule of phenylhydrazine in hot dilute alcohol containing some acetic acid, gave a compound melting at 127–8°. It is slowly dissolved in aqueous alkalies with the probable saponification of the acetyl radical. It is soluble in alcohol and less so in ether and chloroform; insoluble in benzene. It was crystallized for analysis from alcohol.

Calculated for $C_{16}H_{16}O_3N_2$: N, 9.86.
Found: N, 9.38.

The action of phenylhydrazine on resacetophenonediacetate[3] as well as the action of hot acetic anhydride on the phenylhydrazone of resacetophenone, gave a thick, viscous product, which could not be obtained in a crystalline form.

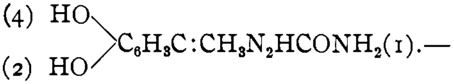
Mononitroresacetophenone Phenylhydrazone,



$\left.\begin{matrix}(4)\ HO\\(2)\ HO\end{matrix}\right\rangle C_6H_2NO_2C.CH_3N_2HC_6H_5(1)$.—The phenylhydrazone of mononitroresacetophenone was obtained by dissolving the mononitroresacetophenone[4] in hot alcohol and adding slightly more than one molecule of phenylhydrazine. On cooling, beautiful dark red crystals separated out, which, after crystallization from alcohol and acetic acid, melted at 232–4° with decomposition. It is somewhat soluble in hot benzene or toluene with a brownish color, and in hot alcohol or chloroform with a reddish color. It dissolves in glacial acetic acid with a reddish color and may be precipitated by water. As would be expected, it is soluble in alkalies; the precipitate obtained by neutralizing this solution with hydrochloric acid at first appears yellowish brown, but with an excess of acid rapidly becomes red in color.

Calculated for $C_{14}H_{13}O_4N_3$: N, 14.63.
Found: N, 14.11.

Resacetophenone Semicarbazone,



$\left.\begin{matrix}(4)\ HO\\(2)\ HO\end{matrix}\right\rangle C_6H_3C{:}CH_3N_2HCONH_2(1)$.—

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[1] Torrey and Kipper: THIS JOURNAL, **29**, 80.

[2] *J. pr. Chem.* [2], **23**, 149; *Am. Chem., J.*, **7**, 276.

[3] *Ber.*, **30**, 297.

[4] *J. pr. Chem.* [2], **23**, 151.

An aqueous solution containing rather more than one molecule of semicarbazide hydrochloride, together with an equivalent quantity of sodium acetate, was added to one molecule of resacetophenone dissolved in alcohol. The mixture was shaken for some time. After filtration the reaction product was dried on a porous plate and crystallized from benzene. Yellow needles, melting with gradual decomposition at 214–220°, were obtained. The semicarbazone is soluble in alcohol, ether, and hot benzene, and is soluble in chloroform. It is soluble in ammonia and aqueous alkalies.

Calculated for $C_9H_{11}O_3N_3$: N, 20.09.
Found: N, 19.34.

The Preparation of Resodiacetophenone.—The method used for making resodiacetophenone was essentially that employed by Crespieux.[1] One and one-half molecules of anhydrous zinc chloride were dissolved in one and one-half molecules of glacial acetic acid, and to this hot mixture one molecule of resacetophenone was added, after which the whole was heated to 140° in an oil-bath. From a dropping funnel one molecule of phosphorus oxychloride was run slowly into the mixture, while the heating at 140° was continued for one-half hour. The hot, viscous product was then poured into water; the resodiacetophenone separating out was filtered from the soluble zinc salts and crystallized from alcohol. It was found that a shorter heating (3–5 minutes) at 140–150° after the addition of the phosphorus oxychloride was advantageous. While adding the phosphorus oxychloride care must be taken not to allow the temperature to rise above 150°, as carbonization is likely to take place. A mixture of alcohol and benzene was found more advantageous than pure alcohol for the crystallization of the resodiacetophenone, as it was found easier to separate it from a reddish substance, probably resacetëin, formed at the same time. When the latter had been formed in considerable amounts, benzene was used with advantage as a crystallizing medium, as the red-colored impurity is practically insoluble even in hot benzene. It is desirable, however, to carry out the first crystallization in alcohol. By fusing resorcinol diacetate with anhydrous zinc chloride, J. F. Eijkmann[2] obtained a diacetodihydroxyphenone, which proves to be identical with the resodiacetophenone made according to the method given above. Eijkmann[3] showed that the same methoxyethoxydiacetophenone was obtained in each case, whether the methoxyhydroxydiacetophenone was ethylated or the ethoxyhydroxydiacetophenone was methylated; further, by oxidation of dimethoxydiacetophenone with potassium permanganate, 4,6-dimethoxyisophthalic acid, $C_6H_2(COOH)_2^{1,3}(OCH_3)_2^{4,6}$,

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[1] *Bull. Soc. Chim.* [3], 6, 152.

[2] *Chem. Centr.*, **1904**, I, 1597

[3] *Ibid.*, **1905**, I, 814.

was obtained, showing conclusively the constitution of the dihydroxydiacetophenone to be $C_6H_2(COCH_3)_2{}^{1.5}(OH)_2{}^{2.4}$.

The identity of resodiacetophenone, made as given above, with this dihydroxydiacetophenone, was shown by making the mono- and dimethyl ethers by the action of methyl iodide on an alcoholic solution of the potassium salt of resodiacetophenone. These melting-points were found to be 120° and 170°, respectively, the same as given by Eijkmann. Further, the phenylhydrazones of both compounds were found to be identical in properties.

Salts of Resodiacetophenone.—Resodiacetophenone, when dissolved in that quantity of sodium hydroxide which gave two molecules of the latter to one of the former, and evaporated to dryness on the steam-bath, gave the white sodium salt. If lead acetate was added to some of the above solution, a pinkish precipitate of the lead salt was obtained. The addition of silver nitrate gave a white precipitate which blackened rapidly in the air.

Resodiacetophenone Bisphenylhydrazone, 2,4-Dihydroxy-1,5-Diacetophenone Bisphenylhydrazone, $C_6H_2(OH)_2(C.CH_3N_2HC_6H_5)_2$.—This substance was discovered by Crespieux[1] and has been described by us also in a recent paper.[2] It is best prepared by allowing considerably more than two molecules of phenylhydrazine to stand for several hours with an alcoholic solution of resodiacetophenone. The substance crystallized from aniline, diethyloxalate, acetone and alcohol, all gave the same melting-point, namely 291°. This is 60° higher than that given by Crespieux. Work which is now being carried on in the laboratory by Mr. R. D. Bell and one of us has shown that varying quantities of resodiacetophenone monophenylhydrazone are formed together with the bisphenylhydrazone, even when a large excess of phenylhydrazine is used and the mixture is allowed to stand for some time. Such mixtures melt at about 230°, but after treatment with a sodium hydroxide solution, which dissolves out the monophenylhydrazone without having the slightest effect upon the bisphenylhydrazone, the melting-point is immediately raised. That it is the resodiacetophenone monophenylhydrazone which is dissolved out by the alkali was shown by precipitating the filtrate with acid and analyzing the product after crystallization from diethyl oxalate. The insolubility of resodiacetophenone bisphenylhydrazone in even the most concentrated aqueous alkalies is very marked. It is, however, easily soluble in alcoholic sodium or potassium hydroxide, giving a yellow solution, from which the original compound, together with small quantities of a decomposition product, namely, the monophenylhydrazone, may be precipitated by mineral acids. If acetic acid was

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[1] *Bull. Soc. Chim.* [3], 6, 152.

[2] THIS JOURNAL, 29, 80.

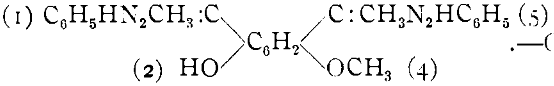
used, instead of hydrochloric, the precipitate, as it stood in the liquid, appeared almost white. The modification obtained by crystallization from aniline had a rather deep orange color.

The Monophenylhydrazone of Resodiacetophenone, 2,4-Dihydroxy-1,5-Diacetophenone Monophenylhydrazone, $C_6H_2(OH)_2COCH_3.CCH_3NNHC_6H_5$. —This compound was obtained exactly as the bisphenylhydrazone, except that only a little more than one molecule of phenylhydrazine to one of resodiacetophenone was employed. The light yellow crystals which separated out were collected on a filter, washed, and then dissolved in 10 per cent. sodium hydroxide, to free them from the small amount of bisphenylhydrazone formed, which is insoluble in aqueous alkalies. After filtration the hydrazone was precipitated with hydrochloric acid. The precipitate was washed with hot water and finally with alcohol, dried on a porous plate and crystallized from brombenzene, in which the monohydrazone is very soluble when hot and but slightly so in the cold. Light yellow needles, melting with decomposition at 233°, were obtained. By crystallization from hot acetone, in which the solubility is also high, yellow, tetragonal plates were formed, likewise melting at 233°.

Calculated for $C_{16}H_{16}O_3N_2$: N, 9.86.
Found: N, 9.58.

This monohydrazone is soluble in ammonia and aqueous alkalies with a yellow color. It is soluble in acetic acid, hot and cold, and precipitated from this solution by water. It is slightly soluble in hot or cold alcohol, benzene, or chloroform, and readily soluble in hot acetone and ethyl acetate.

Bisphenylhydrazone of the Monomethylether of Resodiacetophenone,



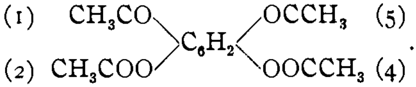
$$\begin{matrix} (1)\ C_6H_5HN_2CH_3{:}C & & C{:}CH_3N_2HC_6H_5\ (5) \\ & C_6H_2 & \\ (2)\ HO & & OCH_3\ (4) \end{matrix}$$

.—One molecule of the monomethyl ether of resodiacetophenone, dissolved in hot alcohol, was heated on a steam-bath for a short time with slightly more than two molecules of phenylhydrazine. A light yellow precipitate began to appear very soon, and after cooling and allowing to stand for a few hours, an almost quantitative yield of the hydrazone was obtained. It was crystallized from benzene, in which it is quite soluble when hot. Long, transparent needles were obtained, melting at 245–6°, with decomposition, which were insoluble in aqueous alkalies.

Calculated for $C_{23}H_{24}O_2N_4$: N, 14.43.
Found: N, 14.18.

When the dimethyl ether of resodiacetophenone was treated with phenylhydrazine in hot or cold alcohol or in alcohol and acetic acid, no action took place, as the product, after crystallization from dilute alcohol, proved to be merely unchanged resodiacetophenone dimethyl ether.

Resodiacetophenone Diacetate (1,5-Diacetophenone Diacetate-2,4),

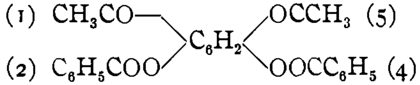


$$\begin{matrix}(1)\ \mathrm{CH_3CO} & & \mathrm{OCCH_3}\ (5)\\ & \mathrm{C_6H_2} & \\ (2)\ \mathrm{CH_3COO} & & \mathrm{OOCCH_3}\ (4)\end{matrix}$$

.—Five grams of resodiacetophenone were dissolved in about 30 grams of acetic anhydride and boiled for two hours under a reflux condenser. The solution was allowed to cool and filtered from the precipitate which separated. After drying and crystallization from alcohol, colorless needles, melting at 120°, were obtained, while from benzene the compound crystallized in transparent hexagonal plates. It is readily soluble in chloroform and in hot alcohol or benzene, and is far more soluble in cold benzene than is resodiacetophenone.

Calculated for $C_{14}H_{14}O_6$:	C, 60.43; H, 5.04.
Found:	C, 60.15; H, 5.56.

Resodiacetophenone Dibenzoate (1,5-Diacetophenone Dibenzoate),

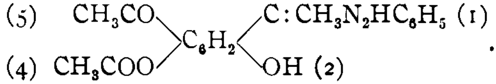


$$\begin{matrix}(1)\ \mathrm{CH_3CO—} & & \mathrm{OCCH_3}\ (5)\\ & \mathrm{C_6H_2} & \\ (2)\ \mathrm{C_6H_5COO} & & \mathrm{OOCC_6H_5}\ (4)\end{matrix}$$

.—It was found possible to prepare the dibenzoate by heating resodiacetophenone with benzoyl chloride at 170–180°, but much better results were obtained by the following method, which gave an almost quantitative yield: Five grams of resodiacetophenone were dissolved in thirty grams of warm pyridine, the solution was then cooled in ice-water, at which temperature some resodiacetophenone separated, and a little more than two molecules of benzoyl chloride were added in small portions with constant shaking. The mixture was then allowed to come to room temperature and finally heated just enough to make the solution complete. After allowing to cool again, first water and then a solution of sodium carbonate were added and the dibenzoate was washed with ammonia. Drying and crystallization from alcohol gave a constant melting-point of 118–9°. It is soluble in benzene, alcohol and chloroform, but more so in the hot than in the cold solvent; it is also soluble in hot and cold glacial acetic acid and very soluble in hot toluene. It is readily saponified by boiling with a ten per cent. sodium hydroxide solution.

Calculated for $C_{24}H_{18}O_6$:	C, 71.64; H, 4.48.
Found:	C, 71.48; H, 5.25.

Monophenylhydrazone of Resodiacetophenone Monoacetate,

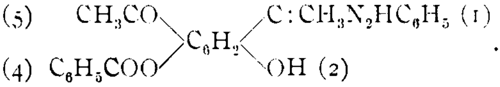


$$\begin{matrix}(5)\ \mathrm{CH_3CO} & & \mathrm{C{:}CH_3N_2HC_6H_5}\ (1)\\ & \mathrm{C_6H_2} & \\ (4)\ \mathrm{CH_3COO} & & \mathrm{OH}\ (2)\end{matrix}$$

.—Two molecules of phenylhydrazine were allowed to act on one of resodiacetophenone diacetate dissolved in a mixture of hot acetic acid and alcohol. On cooling, a heavy white precipitate fell, which after filtration, drying on a porous plate, and crystallization from benzene, was obtained in the form of transparent plates, melting, when pure, at 191-2°; from alcohol it crystallized in white needles, giving the same melting-point. In the mother liquor, from the preparation of this compound, acetylphenylhydrazine,[1] $C_6H_5NHNHCOCH_3$, was isolated, proving that one at least of the acetyl groups must have split out. The interference of these groups is shown in an even more marked degree by the action of four molecules of phenylhydrazine, when both acetyl groups are removed and the bisphenylhydrazine of resodiacetophenone is formed. The monophenylhydrazone of resodiacetophenone monoacetate is rather soluble in hot alcohol and benzene, but only slightly so in these solvents when cold; very soluble in hot toluene; soluble in glacial acetic acid, and precipitated with water. It dissolves slowly in cold sodium hydroxide, rapidly on boiling, with decomposition. By acidification of the solution from the action of either hot or cold hydroxide, resodiacetophenone monophenylhydrazone, m. p. 233°, was obtained. Since the solution has the odor of phenylhydrazine, it is evident that a small amount of this group is also split out.

Calculated for $C_{18}H_{18}O_4N_2$: N, 9.59.
Found: N, 8.70, 9.15.

Monophenylhydrazone of Resodiacetophenone Monobenzoate.

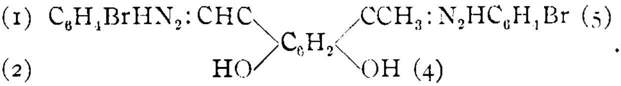


$$\begin{matrix}(5)\ CH_3CO \\ (4)\ C_6H_5COO\end{matrix} > C_6H_2 < \begin{matrix}C:CH_3N_2HC_6H_5\ (1) \\ OH\ (2)\end{matrix}$$

.—The action of phenylhydrazine on the dibenzoate of resodiacetophenone is exactly analogous to its action on the diacetate described above. Two molecules of phenylhydrazine react with one molecule of the dibenzoate in hot alcoholic solution, and on cooling a white compound separates, which after crystallization from alcohol finally gives colorless, transparent prisms, with constant melting-point of 214-5°. The compound is soluble in hot alcohol, benzene and chloroform, but less so in the cold. It may be precipitated from its acetic acid solution by water. It is insoluble in ammonia and in ten per cent. sodium hydroxide, the solvent action is very slow in the cold, but rather rapid on boiling, when doubtless saponification takes place. It will be seen that in the formation of this hydrazone, one benzoyl group has been removed by the action of the phenylhydrazine.

Calculated for $C_{23}H_{20}O_4N_2$: N, 7.22.
Found: N, 7.23, 7.49.

Resodiacetophenone Bisparabromphenylhydrazone.



$$\begin{matrix}(1)\ C_6H_4BrHN_2:CHC \\ (2)\qquad HO\end{matrix} > C_6H_2 < \begin{matrix}CCH_3:N_2HC_6H_4Br\ (5) \\ OH\ (4)\end{matrix}$$

.—An alcoholic solution of two molecules of *p*-bromphenylhydrazine and one of resodiacetophenone was boiled on the steam-bath under a reflux condenser for one

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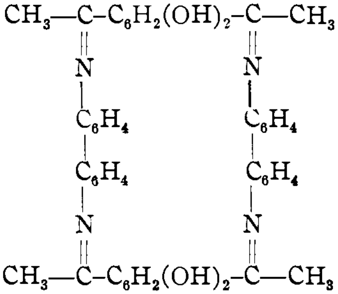
[1] *Ann.*, 190, 129.

hour. The light yellow needles thus obtained were purified by crystallization from acetone, in which the compound is fairly soluble in the hot and less so in the cold. It melted at 270–1° with decomposition. It is readily soluble in hot nitrobenzene, aniline and monobrombenzene, but slightly so in these solvents when cold; insoluble in alcohol, benzene, chloroform, toluene, ligroin, and amyl alcohol; slightly soluble in hot acetic acid and ethyl acetate. It is insoluble in ammonia and aqueous alkalies, but soluble in alcoholic sodium hydroxide; boiling with very strong potassium hydroxide (1 : 1) causes decomposition.

Calculated for $C_{22}H_{20}O_2N_4Br_2$: Br, 30.07.
Found: Br, 29.88.

Addition and Substitution Products Obtained from the Interaction of Resodiacetophenone and Benzidine.—One molecule of resodiacetophenone was dissolved in hot alcohol and to this a hot alcoholic solution of two molecules of benzidine was added and the mixture was heated for about one hour on the steam-bath under a reflux condenser. A precipitate of yellow crystals was obtained which was filtered while the liquid was still hot and was washed with hot alcohol. This product, which melted above 300° was insoluble in the ordinary solvents, but soluble in hot aniline, monobrombenzene or nitrobenzene, the last two solvents causing a slight browning; it is not decomposed by ammonium hydroxide, but hot acetic acid causes gradual decomposition and boiling with a ten per cent. sodium hydroxide solution decomposes it slowly and concentrated hydrochloric acid causes a fairly rapid hydrolysis. From aniline, light yellow needles, melting above 300°, were obtained, which proved, on analysis, to be a condensation product of benzidine and resodiacetophenone in the proportion of one molecule of each. Because of the marked insolubility in all the ordinary solvents, no attempt was made to determine the molecular weight. Since in condensation of benzidine with aldehydes and ketones both amine groups commonly enter into the reaction and from analogy to the azine derivative described below, it appears most likely that two molecules of benzidine have reacted with two molecules of resodiacetophenone, giving a compound of the following formula:



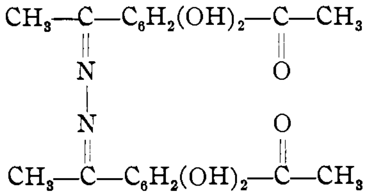
$$\begin{array}{lcccl} CH_3- & C & -C_6H_2(OH)_2- & C & -CH_3 \\ & \Vert & & \Vert & \\ & N & & N & \\ & \vert & & \vert & \\ & C_6H_4 & & C_6H_4 & \\ & \vert & & \vert & \\ & C_6H_4 & & C_6H_4 & \\ & \vert & & \vert & \\ & N & & N & \\ & \Vert & & \Vert & \\ CH_3- & C & -C_6H_2(OH)_2- & C & -CH_3 \end{array}$$

Calculated for $C_{44}H_{36}O_4N_4$: C, 77.19; H, 5.26; N, 8.19.
Found: C, 77.31; H, 5.82; N, 8.22.

From the alcoholic filtrate from the preparation of the above benzidine derivative, yellow needles separated on cooling, which were washed with cold alcohol. These melted slowly between 182° and 185° with decomposition; a second and a third rapid crystallization from alcohol gave the same melting-point, as well as crystallization from benzene. Since the two reacting substances, benzidine and resodiacetophenone, are both colorless, and the product obtained consisted of beautiful, well-shaped, yellow crystals, it is not possible that it is simply a mixture of these two substances. It is readily decomposed on standing with aqueous ammonia or acetic acid, with the former benzidine being precipitated and resodiacetophenone passing into solution, while with the latter resodiacetophenone is precipitated and benzidine dissolved. On boiling the alcoholic or benzidine solution of the low-melting derivative for several hours under a reflux condenser, a yellow precipitate is formed, having the properties of the high-melting condensation product. The properties and the analysis of the soluble low-melting compound indicate that it is an addition product of one molecule of benzidine with four molecules of resodiacetophenone.

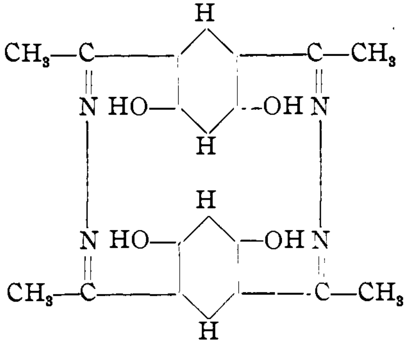
Calculated for $C_{12}H_{12}N_2.4C_{10}H_{10}O_4$: N, 2.92.
Found: N, 2.36, 2.64.

The Mono- and bis-Azine Derivatives of Resodiacetophenone and an Aniline Condensation Product Obtained from the Former.—Considerably in excess of two molecules of hydrazine hydrochloride were allowed to act on one molecule of resodiacetophenone on the steam-bath under a reflux condenser in a 1 : 1 aqueous alcoholic solution to which sodium acetate in an amount equivalent to the hydrochloride had been added. The heavy, yellow precipitate which formed was collected on a filter and washed first with hot water and then with alcohol and dried by suction and plating. This derivative, although soluble in alkalies, is highly insoluble in the common low-boiling organic solvents, but is soluble in hot nitrobenzene or aniline; with the latter, however, a further condensation takes place, as described below. Purification by dissolving in ten per cent. sodium hydroxide and precipitation by hydrochloric acid gave a compound which does not melt under 300° but which changed from yellow to light red between 240° and 260°, and back again to the yellow modification on cooling. Analysis shows that it is monazine of resodiacetophenone, in which one molecule of hydrazine has condensed with two molecules of the ketone:



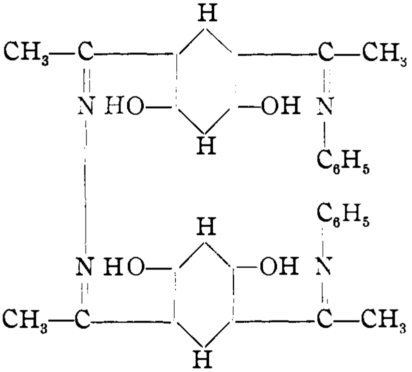
Calculated for $C_{20}H_{20}O_6N_2$: N, 7.29.
Found: N, 7.07.

By carrying out the reaction between hydrazine hydrochloride and resodiacetophenone with a solution of sodium hydroxide instead of sodium acetate, complete condensation between two molecules of hydrazine and two molecules of resodiacetophenone takes place. When sodium acetate is used, the marked insolubility of the first condensation product probably prevents any further reaction. In the reaction in alkaline solution a ten per cent. aqueous sodium hydroxide was used at the temperature of the steam-bath, the alkali-soluble azine compound was precipitated out with hydrochloric acid and dried by plating and suction. The solubilities were found to be about the same as for the monoazine derivative. At 150° the red modification begins to appear, and is much deeper in hue. A small amount kept between this temperature and 300° for about twenty minutes, and then allowed to cool, returns again to the yellow form. On heating in a mixture of acetic and hydrochloric acids, both azine derivatives are decomposed; resodiacetophenone was recovered from the solutions by diluting with water. Analyses of the compound gave results which correspond with the following formula, a bisazine of resodiacetophenone:



Calculated for $C_{20}H_{20}O_4N_4$: N, 14.73.
Found: N, 14.48, 14.43.

On heating the monazine with aniline, further condensation takes place, *viz.*, between two molecules of aniline and the two free carbonyl groups, giving a dianilido monazine of resodiacetophenone, which is insoluble in aqueous alkalies.



Calculated for $C_{32}H_{30}O_4N_4$: N, 10.48; C, 71.91; H, 5.62.
Found: N, 10.97, 10.65, 10.66; C, 71.74; H, 4.54.

Action of Bromine on Resodiacetophenone.—The direct action of bromine on acetophenone[1] gives the ω-bromaceto derivatives, while in the action of bromine on paeonol acetate in carbon disulphide, some of the bromine goes into the side chain, giving exo-brompaeonol acetate, $C_6H_3(OCH_3)_2OCOCH_3COCH_2Br$, and at the same time esobrompaeonol, $OHC_6H_2BrOCH_3COCH_3$, is formed by the action of bromine on the paeonol formed by saponification of the acetate by hydrobromic acid.[2] In studying the action of bromine on resodiacetophenone, we found difficulty in obtaining satisfactory results, since by no variation of the method of preparation or purification could a compound of sharp melting-point be obtained. We have, however, obtained a monobrom derivative in a fair degree of purity and this seems pretty certain to be a ring and not a side-chain substitution product. One molecule of bromine was added to one of resodiacetophenone and the mixture was allowed to stand for six or eight hours with occasional stirring until hydrobromic acid ceased to be evolved. A white, crystalline product was obtained which, after numerous crystallizations from chloroform and alcohol, failed to give a sharp melting-point, gradual liquefaction taking place between 197–202°. Analysis, however, gave a satisfactory result for a monobrom derivative.

Calculated for $C_{10}H_9O_4Br$: Br, 29.31.
Found: Br, 29.38.

Some of the product was allowed to stand with a ten per cent. sodium hydroxide solution for several hours and was finally thrown out of solution with hydrochloric acid. The precipitate had a light yellow color, which crystallization from chloroform did not change and the melting-point was still not sharp, 200–3°. Analysis showed that practically

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[1] *Ber.*, 10, 2006.

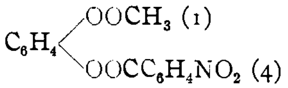
[2] *Ibid.*, **30**, 299.

no bromine had been removed by this treatment, which points to substitution in the ring rather than in the side chain. Found, 28.80 per cent. bromine. When the bromination was carried on in chloroform or when several molecules of bromine were used, the products contained large quantities of bromine, much of which could be removed by treatment with alkalies. The products obtained by bromination had a very strong action on the mucous membrane. On treatment with potassium hydroxide, this action was entirely destroyed.

Bromresodiacetophenone Bisphenylhydrazone, $C_6HBr(OH)_2(C:CH_3N_2HC_6H_5)_2$.—About two molecules of phenylhydrazine were added to one molecule of the monobrom resodiacetophenone dissolved in hot alcohol. On standing for a few hours, the bisphenylhydrazone separated out in beautiful light yellow crystals, slightly soluble in hot benzene and toluene and almost insoluble in alcohol and ether. Crystallized from chloroform, the compound decomposes at 215–20°. It is insoluble in ten per cent. sodium hydroxide in the cold; on heating it dissolves with saponification of a phenylhydrazine group, made evident by the odor of free phenylhydrazine. The phenylhydrazone of the bromresodiacetophenone which had been treated with alkali was also made and the same light yellow product was obtained.

Calculated for $C_{22}H_{22}O_2N_4Br$:	Br, 17.66.
Found:	Br, 17.86.

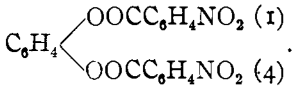
In connection with our work on the dihydroxybenzophenones, we attempted to obtain nitro derivatives by the action of acid chlorides of the nitrobenzoic acids on the acetate, benzoate, nitrobenzoate, and methyl ether of hydroquinone in the presence of various catalyzing agents, as the chlorides of aluminum, zinc or copper. In no case, however, did we obtain benzophenones, but with the acetates found that one or more of the acetyl groups had been replaced by nitrobenzoyl groups. Thus the action of two molecules of nitrobenzoyl chloride on one molecule of hydroquinone diacetate in the presence of anhydrous aluminium chloride at 130–140° gave, besides a small amount of unchanged nitrobenzoyl chloride, two compounds which were readily separated from each other by their different solubilities. After allowing the reaction to proceed for about two hours with occasional additions of aluminium chloride, the reaction product was treated with very dilute hydrochloric acid and finally with a little ammonia to free it from nitrobenzoic acid. After drying on a porous plate, the portion soluble in alcohol was extracted and crystallized from this solvent, in which it is quite soluble when hot and somewhat less so in the cold; its solubility in benzene is similar. The melting-point was 113°. It is insoluble in cold aqueous alkalies, but dissolves rather rapidly on heating. Analysis shows that the compound is hydroquinone monoacetatemononitrobenzoate, one acetyl derivative having been replaced by the nitrobenzoyl group,



$$C_6H_4\left\langle\begin{array}{l}OOCH_3\ (1)\\ OOCC_6H_4NO_2\ (4)\end{array}\right.$$

Calculated for $C_{15}H_{11}O_6N$: C, 59.80; H, 3.65; N, 4.65.
Found: C, 59.18; H, 4.02; N, 4.63.

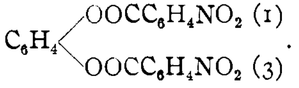
That portion of the product insoluble in alcohol was found to be insoluble also in most of the common organic solvents. It was found possible, however, to crystallize it from hot acetic anhydride, from which it is deposited in small white needles. It is very soluble in hot nitrobenzene and but slightly so in the cold solvent; it is somewhat less soluble in hot diethyl oxalate than in hot nitrobenzene. The melting-point was 268°. Condensation of two molecules of *m*-nitrobenzoyl chloride or the free acid and one of hydroquinone in the presence of phosphorus oxychloride gave the same compound. It is slowly saponified by alcoholic potash, giving some *m*-nitrobenzoic acid. The method of preparation, the saponification product and the analyses show the compound to be hydroquinone-*m*-nitrodibenzoate,



$$C_6H_4\left\langle\begin{array}{l}OOCC_6H_4NO_2\ (1)\\ OOCC_6H_4NO_2\ (4)\end{array}\right. .$$

Calculated for $C_{20}H_{12}O_8N_2$: C, 58.82; H, 2.94; N, 6.86.
Found: C, 58.63; H, 4.19; N, 6.62.

Resorcinol *m*-nitrodibenzoate was formed in a similar attempt to prepare the benzophenone, and likewise by the direct action of *m*-nitrobenzoyl chloride on resorcinol. In this case mere heating on the steam-bath for a few hours gave a completed reaction, while with hydroquinonol a temperature of 130° was required. The solubilities are similar to those of the analogous hydroquinonol derivative. It was crystallized from nitrobenzene, m. p. 172°. Analysis gave results for resorcinol *m*-nitrodibenzoate,

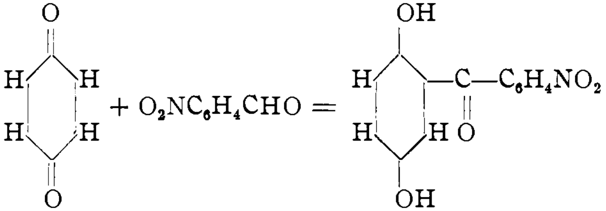


$$C_6H_4\left\langle\begin{array}{l}OOCC_6H_4NO_2\ (1)\\ OOCC_6H_4NO_2\ (3)\end{array}\right. .$$

Calculated for $C_{20}H_{12}O_8N_2$: C, 58.82; H, 2.94; N, 6.86.
Found: C, 58.47; H, 3.27; N, 6.69.

The action of *m*-nitrobenzoyl chloride on resorcinol dibenzoate in a number of different solvents such as carbon disulphide, phosphorus trichloride and phosphorus oxychloride was tried without result. Orthonitrobenzoyl chloride on resorcinol dibenzoate in the presence of anhydrous zinc chloride and infusorial earth gave entirely unsatisfactory results, while *o*- and *m*-nitrobenzoyl chlorides on resorcinol or hydroquinonol *m*-nitrobenzoate in the presence of various catalyzers, as anhydrous zinc and aluminum chlorides and metallic copper gave no reaction. The dimethyl ether of resorcinol is a derivative in which the substituting groups are comparatively stable and should offer little interference; with *o*-nitrobenzoyl chloride and zinc or aluminum chlorides, however, the acid chloride was decomposed and with *m*-nitrobenzoyl chloride, although hydrochloric acid was given off, it was found that the reaction consisted principally in the replacement of the methyl by the nitrobenzoyl groups. This reaction is in line with the observation of A. Claus[1] that acetyl chloride in the presence of zinc chloride tends to remove the methyl groups in the methyl ether of resorcinol. Since an excellent method for preparing resodiacetophenone is the isomerization of resorcinoldiacetate by means of zinc chloride, an attempt was made to isomerize the resorcinol-*m*-nitrobenzoate; with anhydrous zinc chloride at 130–140° there was no change, and with mixtures of zinc chloride and aluminum chloride or with aluminum chloride alone, carbonization occurred before the desired reaction took place.

Since acetaldehyde[2] and benzaldehyde,[3] acting on quinone, give, beside the acetate and benzoate and quinhydrone, considerable quantities of the dihydroxy aceto- or benzophenone, it was thought possible that the nitrobenzaldehydes might react in a similar way upon quinone, yielding dihydroxynitrobenzophenones:



Accordingly, quinone was dissolved in melted *o*-nitrobenzaldehyde and allowed to stand in the sunlight for several weeks, but no condensation took place, the nitrobenzaldehyde having been isomerized simply to nitrosobenzoic acid, a reaction which G. Ciamician and P. Silber[4] have shown takes place with the former substance under the influence of sunlight. Salicylaldehyde, in the sunlight, acted as a reducing agent on quinone, giving quinhydrone and salicylic acid. The study of alkali-insoluble phenols is being continued in this laboratory.

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[1] *J. pr. Chem.* [2], 53, 39.

[2] *Ber.*, 31, 1214.

[3] *Ibid.*, 24, 1341.

[4] *Ibid.*, 34, 2040.

CAMBRIDGE, MASS.