mixture was subject to sudden rises in temperature and subsequent explosions. Consequently we were obliged to abandon the attempt to show that ether can be quantitatively oxidized under these conditions.

In an effort to check the apparent contradiction in the literature on the effect of chromic anhydride on ether, some pure chromic anhydride was prepared, and added to pure ether. A very violent reaction, with evolution of aldehyde vapors, and separation of green chromic oxide, resulted. When the ether was cooled in a freezing mixture to —10° and the chromic anhydride added, a yellow solution was momentarily produced, but reaction began almost at once with the same results as before.

Summary.

1. Ether vapor is oxidized to aldehyde and acetic acid, when heated with air or oxygen.

2. This oxidation begins at temperatures as low as 110°, and is very rapid at 160°.

3. Chromic anhydride does not dissolve without alteration in pure ether.

FORT COLLINS, COL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

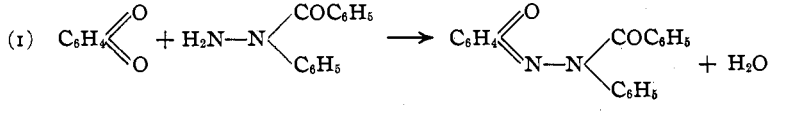
A CONTRIBUTION TO THE STUDY OF THE CONSTITUTION OF THE HYDROXYAZO COMPOUNDS. THE ACTION OF UNSYMMETRICAL BENZOYLPARATOLYLHYDRAZINE UPON BENZOQUINONE AND ITS HOMOLOGS.

BY WILLIAM McPHERSON AND GEORGE WEATHERWORTH STRATTON.

Received March 6, 1915.

Theoretical.

It has been shown by Nef and McPherson[1] that unsymmetrical (or α) benzoylphenylhydrazine condenses with paraquinones forming the corresponding quinonehydrazones. For example, with benzoquinone the reaction is represented by the following equation:

(1) 

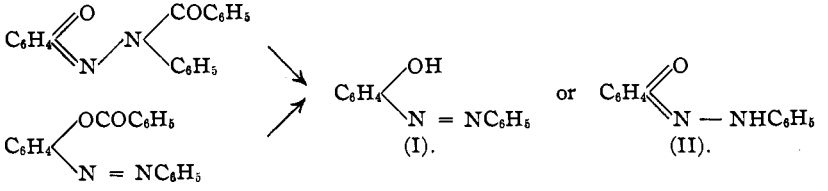
The resulting hydrazones proved to be, not identical, but isomeric with the benzoyl derivatives of the corresponding hydroxyazo-compounds. Thus the hydrazone obtained by the action of unsymmetrical benzoylphenylhydrazine on benzoquinone according to Equation 1 given above, is isomeric with the benzoyl derivative of hydroxyazobenzene prepared by the reaction expressed in the following equations:

[1] *Ber.*, **28**, 2418 (1895); *Am. Chem. J.*, **22**, 364 (1899); **25**, 485 (1901).

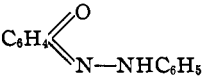
(2) (a) $C_6H_5ONa + C_6H_5N_2Cl \longrightarrow C_6H_4(ONa)(N=NC_6H_5) + HCl$

(b) $C_6H_4(ONa)(N=NC_6H_5) + C_6H_5COCl \longrightarrow C_6H_4(OCOC_6H_5)(N=NC_6H_5) + NaCl$

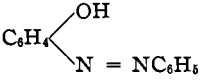
Now both the hydrazone derivative formed as represented in Equation 1 above and the isomeric hydroxyazo compound formed according to Equation 2 yield on saponification the same compound, namely, hydroxyazobenzene (benzeneazophenol). The reactions are represented by the following equations:

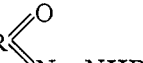


It is evident, therefore, that in the saponification of one of the compounds a migration of the hydrogen atom replacing the benzoyl group takes place. If the migration occurs in the hydrazone, the hydrogen atom which takes the place of the benzoyl group passing from the nitrogen to the oxygen, then the constitution of the resulting hydroxyazobenzene must be represented by Formula I. On the other hand if the migration takes place in the hydroxyazo compound then Formula II correctly represents the constitution of the hydroxyazobenzene. From the general results obtained in different investigations,[1] it seems probable that the migration actually takes place in the hydrazone and that Formula I is the correct one for hydroxyazobenzene. This indicates that the molecule represented by the formula



is unstable, rearranging as fast as formed to the more stable compound

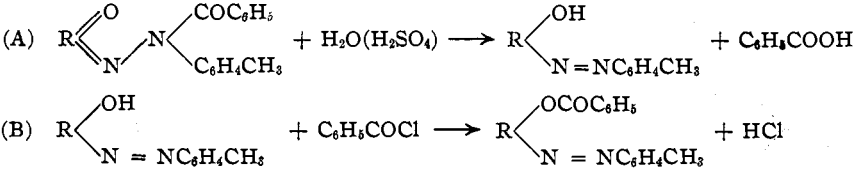


It was thought that by varying the radicals it might be possible to obtain a stable body of the general formula,  and consistent efforts have been made in this laboratory to isolate a compound of this constitution. If such a compound could be isolated, it would throw much light upon the general question of the constitution of the parent

[1] THIS JOURNAL, 33, 1525.

hydroxyazo compounds. In the present investigation, the action of the unsymmetrical benzoyl-*p*-tolylhydrazine upon some of the *p*-quinones was investigated. It was found that hydrazones are formed in accordance with the following equation:

The resulting hydrazones when saponified yield not the parent hydrazones, but hydroxyazo compounds (Equation A) and these when benzoylated (Equation B) give derivatives that are not identical but isomeric with the original benzoylhydrazones:



Experimental Part.

Preparation of *p*-Tolylhydrazine.—This is most readily obtained from *p*-toluidine by methods similar to those used in preparing phenylhydrazine from aniline. The following method gave good results: To 18 g. of *p*-toluidine was added 150 cc. of water and then 30 cc. of hydrochloric acid (sp. gr. 1.2). The resulting mixture was then stirred until all of the toluidine dissolved. The clear liquid so obtained was cooled to 5° and diazotized by the addition of the theoretical quantity of sodium nitrite (12 g.). To the resulting solution there was added, slowly at first and with constant stirring, 120 g. of stannous chloride dissolved in 100 cc. of concentrated hydrochloric acid. The tolylhydrazine hydrochloride separated out as a thick, white solid. It was removed by filtration and the filtrate salted out to obtain the hydrochloride which remained in solution. The yield of the hydrochloride was from 65 to 75% of the theoretical quantity. In order to obtain the free tolylhydrazine, the hydrochloride was neutralized with a concentrated solution of sodium hydroxide. The tolylhydrazine separated out on the surface of the liquid as a yellow oil which solidified to an almost white solid when the solution cooled. The solid was removed and the remaining solution extracted with ether in order to dissolve out any remaining hydrazine. The crude compound was purified by recrystallizing from ether.

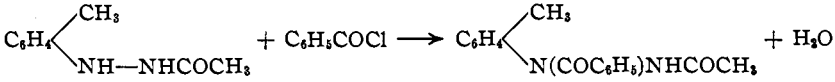
Preparation of β-Acetyl-*p*-tolylhydrazine, $CH_3C_6H_4$—NH—$NHCOCH_3$. —This compound was first prepared by Gattermann, Johnson and Holze[1] by boiling a solution of the tolylhydrazine in glacial acetic acid. The

[1] *Ber.*, **25**, 1080 (1892).

following method was found to give an excellent yield of the pure compound:

The theoretical quantity of acetic anhydride was slowly added to an ethereal solution of 25 g. of the tolylhydrazine. The rapid evaporation of the ether during the reaction keeps the temperature down and gives a pure product. Before all the anhydride was added the acetylhydrazine began to separate, and at the end of the experiment a large percentage of it had settled to the bottom of the vessel. This was filtered from the ether and washed once or twice with ether—a procedure which obviated the troublesome recrystallization from hot water. The pure compound melting at 130° was thus readily obtained.

α-Benzoyl-β-acetyl-*p*-tolylhydrazine, $CH_3C_6H_4N(COC_6H_5)NHCOCH_3$. —Upon benzoylating β-acetyl-*p*-tolylhydrazine in benzene solution by means of benzoyl chloride the benzoyl group enters in the α-position as shown in the following equation:



In carrying out the reaction the acetyl compound was dissolved in benzene (25 g. in 250 cc. of benzene) in a flask which was then connected with a reflux condenser. The theoretical quantity of benzoyl chloride was added through the condenser and the solution boiled until hydrogen chloride ceased to be evolved. The addition of benzoyl chloride causes the formation of a precipitate which dissolves, however, when the mixture is heated.

If the benzene solution is allowed to cool slowly the α-benzoyl-β-acetylhydrazine separates out as a hard cake which adheres firmly to the bottom of the flask. It was found better to pour the hot solution into a beaker, evaporate a portion of the benzene and cool rapidly, constantly agitating the liquid. In this way it was obtained in the form of finely divided crystals. The yield was almost quantitative.

α-Benzoyl-β-acetyl-*p*-tolylhydrazine is very slightly soluble in ligroin, rather more soluble in ether and alcohol and chloroform, and very soluble in benzene. It may be purified by crystallizing from benzene or benzene-ligroin. From these solvents it is obtained in compact nodules of small crystals, which melt sharply at 135°.

Calc. for $C_{16}H_{16}N_2O_2$: N, 10.45; C, 71.64; H, 5.97; found: N, 10.38; C, 71.76; H, 5.96.

α-Benzoyl-*p*-tolylhydrazine, $CH_3C_6H_4—N(COC_6H_5)NH_2$.—This compound is prepared by the saponification of α-benzoyl-β-acetyl-*p*-tolylhydrazine.

The process was carried out as follows: 25 g. of α-benzoyl-β-acetyl-

p-tolylhydrazine was placed in a flask and 150 cc. of water added. The flask was connected with a reflux condenser and the mixture heated to boiling. Alcohol was then poured in, a little at a time, until the solid was just dissolved. Sulfuric acid (25 g.) was then added and the solution boiled until the odor of ethyl benzoate could be detected. As the solution cooled the sulfate of the α-benzoyl-*p*-tolylhydrazine separated. It was always found to be mixed with some unchanged α-benzoyl-β-acetyl-*p*-tolylhydrazine. Different concentrations of sulfuric acid were tried with the idea of eliminating this difficulty, but the most satisfactory results were obtained with the dilution given.

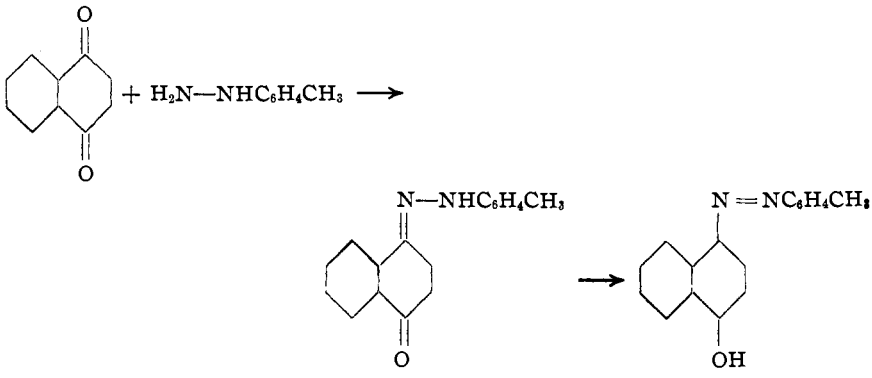
The sulfate obtained by the above process was purified by washing it first with chloroform and then with ether. It is a white solid, but slightly soluble in the common organic solvents excepting alcohol. To obtain the free hydrazine the sulfate was dissolved in dilute alcohol, neutralized with sodium carbonate and the resulting solution extracted with ether. Upon evaporation of the ether an oil was obtained which would not solidify. By extracting this oil several times with ligroin, combining the ligroin extracts and evaporating them slowly, an oil was finally obtained which, on standing for several days, changed almost entirely into fine, white crystals which were grouped together in nodules. They were purified by washing rapidly with ether. The pure α-benzoyl-*p*-tolylhydrazine thus obtained is very soluble in the common organic solvents. It melts at 68–70°.

Calc. for $C_{14}H_{14}N_2O$: N, 12.39; C, 74.34; H, 6.19; found: N, 12.32; C, 73.90; H, 6.25.

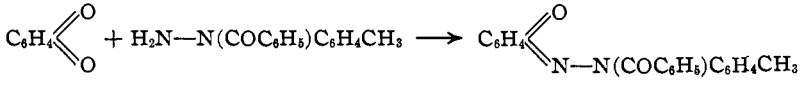
α-Benzoyl-*p*-tolylhydrazinehydrochloride.—The hydrochloride of α-benzoyl-*p*-tolylhydrazine was prepared from the free compound by dissolving the latter in benzene and passing dry hydrogen chloride into the solution. It separated out as a pinkish white solid which was purified by washing with benzene and ether.

The Action of Tolylhydrazine upon *p*-Quinones.—It has long been known[1] that phenylhydrazine acts as a reducing agent upon quinones of the benzene series, converting them into the corresponding hydroquinones. With α-naphthoquinone, on the other hand, condensation takes place and a hydroxyazo compound is produced. It was found that *p*-tolylhydrazine acts in a similar way. Thus by its action in benzene solution, benzo-, tolu- and thymo-quinones are converted into the corresponding hydroquinones, while α-naphthoquinone gives tolueneazo-α-naphthol. In the first three cases nitrogen is evolved and the hydroquinones precipitate on standing. The reaction with α-naphthoquinone is represented by the following equation:

[1] *Ber.*, 16, 1563 (1883).



The Action of α-Benzoyl-*p*-tolylhydrazine Hydrochloride (or Sulfate) on Benzoquinone; Benzoquinone-α-benzoyl-*p*-tolylhydrazone.—The sulfate or hydrochloride of α-benzoyl-*p*-tolylhydrazine condenses with benzoquinone, yielding the corresponding hydrazone:

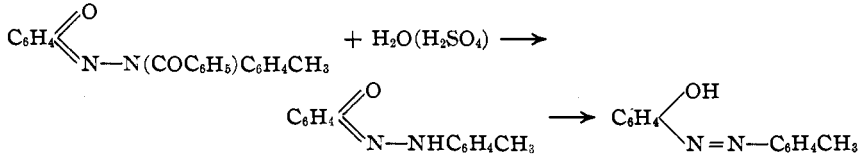


The reaction must be carried out in dilute alcoholic solution, since in concentrated solutions decomposition results.

One gram of benzoquinone was dissolved in 200–250 cc. of 95% alcohol. Water was added to this solution until the total volume was about 600 cc. To this solution was then added 4 g. of α-benzoyl-*p*-tolylhydrazine sulfate dissolved in 600 cc. of dilute alcohol of the same strength as the solvent for the quinone. The mixture was stirred and allowed to stand for 24 hours. The hydrazone separated as a yellowish solid which slowly settled to the bottom of the flask. It was filtered by suction, dried on the hot plate at 100° and recrystallized several times from benzene-ligroin and finally from ligroin. It was thus obtained in the form of finely divided, yellow crystals which melted at 141°. The yield of the crude product was 3 g. The compound is very soluble in ether, alcohol, benzene and chloroform and slightly soluble in ligroin.

Calc. for $C_{20}H_{16}N_2O_2$: N, 8.86; C, 75.95; H, 5.06; found: N, 8.95; C, 75.63; H, 5.07.

Action of Saponifying Agents upon Benzoquinone-α-benzoyl-*p*-tolylhydrazone,

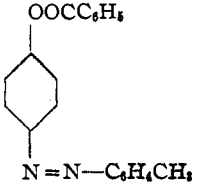


When saponified with hot alcoholic potash or concentrated sulfuric acid

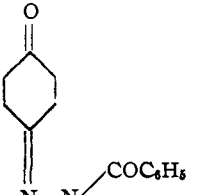
the hydrazone is converted into *p*-tolueneazophenol and benzoic acid as shown in the above equation. The best results were obtained by dissolving the hydrazone in concentrated sulfuric acid and pouring the resulting solution into a large volume of water. The impure phenol separated at once. It was purified by dissolving it in a 20% sodium hydroxide solution, filtering and neutralizing the filtrate with hydrochloric acid. Further purification was accomplished by repeated recrystallization from ligroin and benzene-ligroin. The finely divided orange-yellow crystals thus obtained melted sharply at 152°. This compound was found to be identical with tolueneazophenol prepared by the action of *p*-diazotoluenechloride upon phenol. Each of the two compounds as well as a mixture of the two melted sharply at 152°. All efforts to obtain the free benzoquinone-*p*-tolylhydrazone failed, indicating its probable unstable character.

The Benzoate of *p*-Tolueneazophenol.—This compound was prepared from tolueneazophenol by the Baumann-Schotten reaction. The crude product was purified with ligroin. It forms reddish yellow needles melting at 159°.

This benzoate, according to its method of preparation, must be represented by Formula I below. It is not identical but isomeric with benzoquinone-α-benzoyl-*p*-tolylhydrazone, the constitution of which is represented by Formula II below:



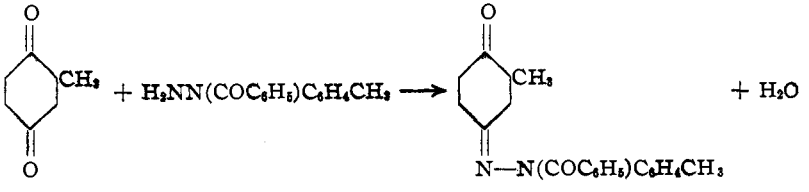
(I)



(II)

The colors and crystalline forms of the two compounds as well as their melting points are different. Moreover, the melting point of a mixture of the two, while indefinite, was considerably below that of either of the pure compounds.

The Action of α-Benzoyl-*p*-tolylhydrazine on Toluquinone; Toluquinone-α-benzoyl-*p*-tolylhydrazone.—The action of the tolylhydrazine on toluquinone takes place according to the following equation:

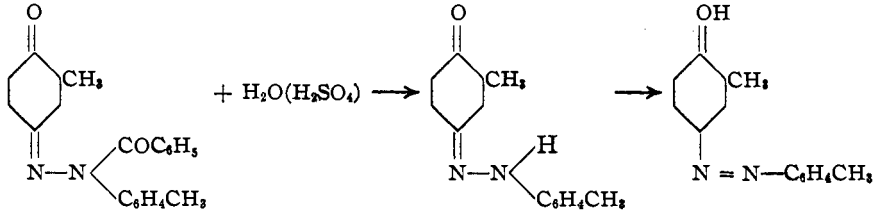


This condensation was effected under the same conditions that were used in the preparation of the corresponding benzoquinonehydrazone.

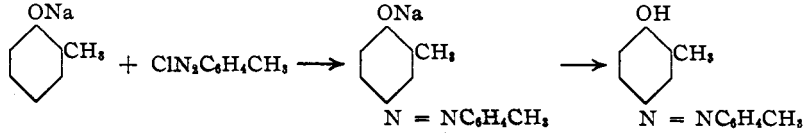
One gram of toluquinone was dissolved in 250 cc. of 95% alcohol and water added until the total volume was about 700 cc. To this solution was then added 3 g. of α-benzoyl-p-tolylhydrazine sulfate dissolved in 700 cc. of dilute alcohol (3 parts of 95% alcohol to 4 parts of water). The hydrazone began to separate at once and at the end of 24 hours the reaction was complete. Two grams of the crude product were obtained. Purification was effected by repeated recrystallization from ligroin and benzene-ligroin. The fine, yellow crystals obtained melted at 178°. They are somewhat lighter in color than the crystals of the corresponding benzoquinone hydrazone. The compound is very slightly soluble in dilute alcohol. It is not very soluble in ligroin but dissolves readily in other organic solvents.

Calc. for $C_{21}H_{18}N_2O_2$: N, 8.49; C, 76.37; H, 5.45; found: N, 8.53; C, 76.16; H, 5.52.

Saponification of Toluquinone-α-benzoyl-p-tolylhydrazone.—The saponification takes place in accordance with the following equation:

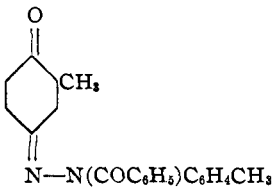


It was effected by dissolving the hydrazone in concentrated sulfuric acid and pouring the resulting solution into a large volume of water. The crude product thus obtained was treated with a 20% caustic potash solution which dissolved the hydroxyazo compound. This was reprecipitated by means of hydrochloric acid, and was purified by repeated crystallization from ligroin. In this way it was finally obtained in the form of orange-yellow crystal clusters melting at 135°. This compound was found to be identical with tolueneazo-o-cresol, prepared by treating a diazotized solution of p-toluidine with an alkaline solution of o-cresol:

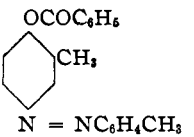


The benzoate of tolueneazo-o-cresol was prepared by the Baumann-Schotten method. By crystallizing from ligroin it was obtained in the form of orange-yellow crystal clusters melting at 165°. It is not identical but isomeric with the compound obtained by the action of α-benzoyl-

p-tolylhydrazine on toluquinone. The formulas of the two compounds are as follows:

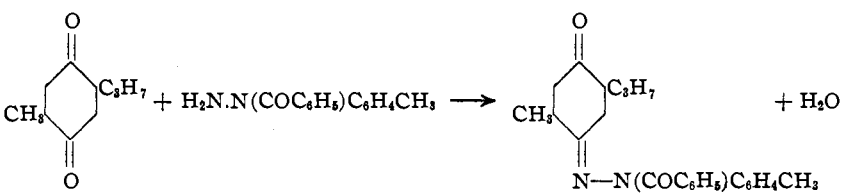


(1) Hydrazone.



(2) Hydroxyazo compound.

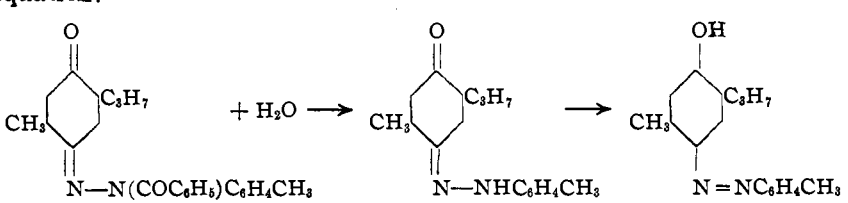
The Action of α-Benzoyl-*p*-tolylhydrazine on Thymoquinone: Thymoquinone-α-benzoyl-*p*-tolylhydrazone.—Thymoquinone condenses with benzoyl-*p*-tolylhydrazine as shown in the following equation:



The condensation was carried out in the following way: One gram of thymoquinone was dissolved in 300 cc. of 95% alcohol and the solution diluted to 700 cc. To this was added 3 g. of α-benzoyl-*p*-tolylhydrazine sulfate dissolved in dilute alcohol (3 parts of 95% alcohol to 4 parts of water). After standing 48 hours the crude hydrazone (1.5 g.) was removed by filtration and purified by repeated crystallizations from ligroin. It was obtained in the form of light yellowish green crystals melting at 125°.

Calc. for $C_{24}H_{24}N_2O_2$: N, 7.53; C, 77.42; H, 6.45; found: N, 7.78; C, 77.25; H, 6.59.

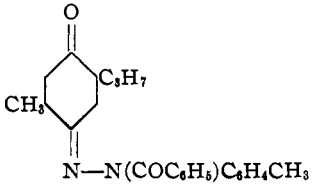
Saponification of Thymoquinone-α-Benzoyl-*p*-tolylhydrazone. — The saponification was effected both by sulfuric acid and by potassium hydroxide. In each case the reaction took place according to the following equation:



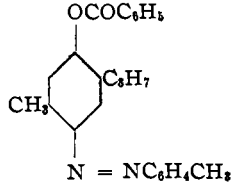
The crude product was dissolved in a dilute solution of potassium hydroxide and reprecipitated by the addition of hydrochloric acid. Finally it was crystallized a number of times from ligroin. It was then obtained in the form of yellow crystals which melted at 117°.

This compound proved to be identical with *p*-tolueneazothymol prepared in the following way: A solution of diazotoluene chloride was added to the theoretical amount of an alkaline solution of thymol. The resulting solid proved to be a mixture of the *o*- and *p*-tolueneazothymol. This mixture was treated with a solution of sodium hydroxide which dissolved the para compound only. This was then precipitated, dried and purified by crystallization from ligroin. The resulting yellow crystalline solid melted at 117°. A mixture of the solid and the product obtained by the saponification of thymoquinonebenzoyl-*p*-tolylhydrazone likewise melted sharply at 117°, thus proving the identity of the two compounds.

Upon benzoylating the tolueneazothymol according to the Baumann-Schotten method, a compound was obtained which crystallized from ligroin in short, red, needle-shaped crystals melting at 127°. A mixture of this compound and thymoquinone-α-benzoyl-*p*-tolylhydrazone melted considerably lower than either constituent. These two compounds are therefore not identical but isomeric as shown in the following formulas:



(1) Hydrazone.



(2) Hydrazo compound.

Summary.

(*a*).—The preparation of α-benzoyl-*p*-tolylhydrazine is given and the properties of the compound described.

(*b*).—The action of α-benzoyl-*p*-tolylhydrazine upon benzoquinone, toluquinone and thymoquinone is described. The resulting compounds are shown to be not identical but isomeric with the benzoyl derivatives of the corresponding compounds prepared by the action of diazotoluene chloride upon phenol, *o*-cresol and thymol, respectively.

(*c*).—The corresponding isomeric compounds when saponified give the same compound, namely, a hydroxyazo compound.

(*d*).—While it is possible to obtain the α-benzoyl derivatives of the quinone hydrazones, no evidence was obtained of the existence of the parent quinone hydrazones in stable form.

(*e*).—The bearing of the reactions upon the constitution of the hydroxyazo compounds is discussed.

COLUMBUS, OHIO.