CLII.—*Hydroxyazo-compounds. The Action of Semicarbazide Hydrochloride on the p-Quinones.*

By ISIDOR MORRIS HEILBRON and JAMES ALEXANDER RUSSELL
HENDERSON.

THE investigations which have been carried out in recent years on quinonehydrazones have shown conclusively that these substances are not quinone derivatives, for where such should be

formed rearrangement invariably seems to take place with the formation of the isomeric hydroxyazo-compounds. Thus, Borsche (*Annalen*, 1907, **357**, 171) found that by condensing *o*-nitrophenylhydrazine with *p*-benzoquinone there resulted, not the quinone-hydrazone (I), but the isomeric hydroxyazo-compound (II):

The spectroscopic evidence, at any rate for the *p*-quinone products, supports the view that where hydrazones might be expected, hydroxyazo-compounds are formed. Tuck (T., 1907, **91**, 449) obtained similar absorption curves for benzeneazophenol (quinonehydrazone) and benzeneazophenetole, which latter substance had been proved by Jacobsen and Fischer (*Ber.*, 1892, **25**, 995) to be a typical azo-derivative, and hence was able to show that the parent substance has the same constitution as the ester, that is, it is a true azo-compound.

The present work, a preliminary account of which was recently published (P., 1912, **28**, 256) was undertaken with a view to examine both by chemical and spectroscopic methods the type of compound produced by the action of semicarbazide hydrochloride on the *p*-quinones, and, as might have been expected, owing to the close resemblance in constitution between hydrazine, phenylhydrazine, and semicarbazide, we are able in this paper to show that the condensation products of semicarbazide with the *p*-quinones are not quinonesemicarbazones, but the isomeric hydroxyazo-formamides.

The knowledge of the quinonesemicarbazones previous to the present work was somewhat meagre. Thiele and Barlow (*Annalen*, 1898, **302**, 315) had found that the compound formed by the action of semicarbazide hydrochloride on *p*-benzoquinone in the proportions necessary for the formation of a monosemicarbazone reacted either as a semicarbazone (III) or as 4-hydroxybenzeneazo-formamide (IV):

The evidence in favour of formula III was the production of a disemicarbazone; on the other hand, by boiling the compound with dilute sodium hydroxide, phenol was produced, the decomposition taking place according to the equation:

In the light of this reaction Thiele and Barlow conclude that *p*-benzoquinonesemicarbazone is a tautomeric substance, in which

a hydrogen atom wanders from the semicarbazone group to the oxygen atom, thus forming hydroxyl, a change which involves an alteration from a quinonoid to a benzenoid structure.

Borsche (*Annalen*, 1904, **334**, 143) reinvestigated the question of tautomerism in some quinonesemicarbazones, but more particularly in the carbamylphenylhydrazone condensation products, and showed that such compounds are apparently tautomeric. The same author also prepared phenetoleazoformamide by the treatment

FIG. 1.

Oscillation frequencies.

of *p*-ethoxyphenylhydrazine with potassium cyanate, followed by oxidation of the product with chromic acid mixture:

a method of preparation proving definitely that the compound is an azo-derivative. The present authors have now prepared this substance directly from benzoquinonesemicarbazone (4-hydroxy-benzeneazoformamide), thus obtaining additional proof of the tautomeric change in the parent compound.

Fig. 1 shows the absorption curve of phenetoleazoformamide in alcohol (full curve) and that of benzeneazophenetole (dotted curve), reproduced from Tuck's paper (*loc. cit.*). The absorption curves are very similar, as is to be expected from two compounds of the same type. That these substances are typical azo-derivatives is

Fig. 2 shows the absorption curves of 4-hydroxybenzeneazo-

18 2000 22 24 26 28 3000 32 34 36 38 4000 42

FIG. 3. *Tetraphenylquinodimethane*.

formamide in alcohol (full curve) and of its acetyl derivative (dotted curve), both of which are identical with the azo-compound, phenetoleazoformamide; hence it is clear, at any rate under the conditions of examination, that *p*-benzoquinonesemicarbazone only exists in its isomeric form as a typical azo-derivative.

The addition of sodium ethoxide to 4-hydroxybenzeneazoformamide causes a complete change in the absorption spectrum, as is shown in Fig. 2 (dot-dash curve). This change in the type of absorption on the addition of sodium ethoxide is common to all the substances examined, as a glance at Figs. 4, 5, 6, and 7 will serve to show.

We have thus direct evidence that the salts of the hydroxyazoformamides are not azo-derivatives, but undoubtedly possess some other structure. A somewhat similar change in absorption on salt formation has been found to occur with *p*-nitrophenol (Baly, Edwards, and Stewart, T., 1906, **89**, 514), the salt of this compound showing an absorption band closely resembling those of the salts of the hydroxyazoformamides. According to these authors, the salts of *p*-nitrophenol are quinonoid, and although in a more recent paper Baly, Tuck, and Marsden (T., 1910, **97**, 571) have rejected this view, other investigators still hold to the quinonoid structure of the nitrophenol salts (compare Hewitt, Pope, and Willett, T., 1912, **101**, 1770; Hantzsch, *Ber.*, 1913, **46**, 1537); hence it may be possible that the salts of the series under investigation are also quinonoid in structure. In order to determine this point, it appeared to us necessary to examine spectrographically some substance possessing undoubted quinonoid structure, as a type of quinone more definite than *p*-benzoquinone (which compound possesses characteristic ketonic properties), and one in which, as in the quinonoid salts in question, the simple isorropic vibration assumed by Baly and Stewart (T., 1906, **89**, 502) to be the cause of colour, was excluded. With this end in view we obtained from Prof. Staudinger, to whom our best thanks are due, a specimen of tetraphenylquinodimethane,

a compound fulfilling the above conditions in all essentials. The absorption curve of this compound in either alcohol or ether is shown in Fig. 3, and, as will be seen, it possesses a characteristic band of considerable persistence with head at about 2300 and a small band in the ultra-violet with head at about 3600 in *M*/10,000-solution, the selective absorption being very similar to that of the hydroxybenzeneazoformamide salts and also to the quinonehydrazone salts obtained by Tuck (*loc. cit.*).

It follows, therefore, that a further change in constitution takes place in the *p*-benzoquinone condensation products on salt formation, for whereas the free substances as examined in solution are typical azo-compounds, the salts are quinonoid in structure.

The same will then apply to the salts of the nitrophenols, the

absorption spectra of which are so similar to that of the typical quinone (tetraphenylquinodimethane) represented in Fig. 3, and thus the principal objection to a quinonoid structure for the salts of the nitrophenols brought forward by Baly, Tuck, and Marsden, namely, that the characteristic band of the salts appeared at a different dilution from that of the quinones cannot be upheld. We suggest, indeed, as a result of this examination of tetraphenylquinodimethane, that the band of benzoquinone and its homologues appearing in $M/10$ -solution is directly due to the diketogroup, such as is present in diacetyl, as this substance gives a similar band to that of *p*-benzoquinone and its homologues.

The exact constitution of the salts has not at present been successfully elucidated, but we suggest, in the meantime, that either formula V or VI may possibly represent a structure in harmony with the experimental evidence, obtained from the study of the absorption spectra of these compounds.

Formula VII, which represents a true quinonoid structure for the salts of hydroxyazoformamides, has also been considered, but is unacceptable for two reasons. In the first place, such a formula is precluded in the similarly constituted salts of the quinone-hydrazones obtained by Tuck (*loc. cit.*), and secondly, with simple semicarbazones, no change in absorption takes place on addition of alkali, as would be expected to occur, if salt formation was produced:

(V.)

(VI.)

(VII.)

Monochloro-p-benzoquinone and Semicarbazide Hydrochloride.

Theoretically, two isomeric hydroxyazo-compounds are possible in this case, as indicated by the formulæ VII and VIII:

(VII.)

(VIII.)

but only one could be isolated, namely, that represented by formula VII, as is proved by the formation of *o*-chlorophenol on

heating with dilute sodium hydroxide. The condensation product in this case reacts only as an azo-compound, no disemicarbazone being formed.

2: 6-Dichloro-p-benzoquinone.—The hydroxyazo-compound formed

FIG. 4.
Oscillation frequencies.

FIG. 5.

FIG. 4. ————— 3-Chloro-4-hydroxybenzeneazoformamide.
 - - - - - " " " + NaOEt.
 3:5-Dichloro-4-hydroxybenzeneazoformamide.
 - - - - - " " " + NaOEt.

FIG. 5. ————— 4-Hydroxy-m-tolueneazoformamide.
 - - - - - " " " + NaOEt.
 4-Hydroxy-3-methyl-5-isopropylbenzeneazoformamide.
 - - - - - " " " + NaOEt.

here is 3:5-dichloro-4-hydroxybenzeneazoformamide, as is proved by the production of 2:6-dichlorophenol on treatment with dilute sodium hydroxide. Neither the isomeric 1:6-dichloro-4-hydroxybenzeneazoformamide nor a disemicarbazone could be obtained.

Fig. 4 represents the absorption curves of the above compounds,

the parent substances in each case being typical azo-derivatives, the salts, on the other hand, showing the characteristic quinonoid graphs.

Toluquinone.—The condensation product in this case is 4-hydroxy-*m*-tolueneazoformamide; one only of the two theoretically possible isomerides was obtained. Proof of this constitution is afforded by the production of *o*-cresol on treatment with alkali. As in the case of the benzoquinone mono-condensation product, 4-hydroxy-*m*-tolueneazoformamide can act tautomerically, a disemicarbazone being obtainable, although in solution, as shown spectrographically in Fig. 5, this compound, like 4-hydroxybenzeneazoformamide itself, exists only as an azo-derivative.

Thymoquinone.—The condensation product was 4-hydroxy-3-methyl-5-isopropylbenzeneazoformamide, yielding thymol with warm sodium hydroxide solution. The compound is a typical azo-derivative, as shown in Fig. 5, and reacts only as such.

Bromination Products of the Hydroxybenzeneazoformamides.

Such compounds are readily obtained by direct action of bromine on the hydroxyazoformamides themselves, mono- and di-bromo-derivatives in several cases being isolated. These bromo-substitution products are typical hydroxyazo-compounds, as is shown by the graphs in Figs. 6 and 7.

In the case of toluquinone and of these chlorinated benzoquinones (which react with semicarbazide), only one of the two theoretically possible isomerides could be isolated, and in each case the azoformamide group is attached to the benzene nucleus remote from the substituents. With thymoquinone the azoformamide group is adjacent to the methyl in preference to the *isopropyl* radicle.

Further, although *p*-benzoquinone and toluquinone form disemicarbazones, monochloro-*p*-benzoquinone, 2:6-dichloro-*p*-benzoquinone and thymoquinone react with only one molecule of semicarbazide, the product formed being essentially an azo-derivative, whilst with 2:5-dichloro-*p*-benzoquinone, trichloro-*p*-benzoquinone, chloroanilic acid, and dibromothymoquinone no reaction took place.

Kehrmann (*Ber.*, 1888, **21**, 3315) found a similar phenomenon when studying the action of hydroxylamine on the substituted quinones, and Staudinger (*Ber.*, 1908, **41**, 1355) observed something similar in studying the action of diphenylketene on the substituted quinones. Whether this inactivity is due to steric hindrance or some other cause remains at present indefinite, but it is evidently general for a large series of various condensation products, further evidence of which is shown in the present case.

Colour Isomerism.—In two cases, namely, with *p*-benzoquinone and 2:6-dichloro-*p*-benzoquinone, red modifications of the condensation product were obtained in addition to the yellow forms. The cause of this difference cannot at present be definitely decided,

FIG. 6.

Oscillation frequencies.

FIG. 7.

FIG. 6. ————— 5-Bromo-4-hydroxy-m-tolueneazoformamide.
 - - - - - " " " " + NaOEt.

FIG. 7. ————— 3-Bromo-4-hydroxy-2-methyl-5-isopropylbenzeneazoformamide.
 - - - - - " " " " " " " " + NaOEt.
 Dibromo-derivative of 4-hydroxy-2-methyl-5-isopropylbenzeneazoformamide.
 - - - - - " " " " " " " " + NaOEt.

but the following possibilities are put forward as probable explanations.

1. The difference in colour may be due to stereoisomerism, in which the two forms may be *syn*- and *anti*-compounds:

2. The difference may be due to structural change, one form being a hydroxyazo-derivative and the other a semicarbazone:

3. The colour difference may be due to valency isomerism in accordance with Hantzsch's views.

4. The difference of colour may be due to dimorphism.

In solution both modifications are identical and exhibit the characteristic absorption of azo-compounds.

The Relation between Molecular Weight and Position of Absorption Band.

In the following table the hydroxyazoformamides are arranged according to their molecular weights, the third column denoting the position of the head of the principal band, and showing that increase in molecular weight tends to push the band towards the red end of the spectrum:

Compound.	Molecular weight.	Head of band.	λ .	Difference from mean value 2174
$\text{C}_7\text{H}_7\text{O}_2\text{N}_3$	165	3000	2165	-9
$\text{C}_8\text{H}_9\text{O}_2\text{N}_3$	179	3000	2179	5
$\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3$	193	3000	2193	19
$\text{C}_7\text{H}_6\text{O}_2\text{N}_3\text{Cl}$	199.5	2950	2167	-7
$\text{C}_9\text{H}_9\text{O}_3\text{N}_3$	207	2950	2174	0
$\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}_3$	221	2900	2154	-20
$\text{C}_7\text{H}_5\text{O}_2\text{N}_3\text{Cl}_2$	234	2900	2167	-7
$\text{C}_8\text{H}_5\text{O}_2\text{N}_3\text{Br}$	258	2900	2191	17
$\text{C}_{11}\text{H}_{14}\text{O}_2\text{N}_3\text{Br}$	300	2800	2167	-7
$\text{C}_{11}\text{H}_{13}\text{O}_2\text{N}_3\text{Br}_2$	379	2700	2179	5
Mean			2174	

FIG. 8.

Fig. 8 shows that the graph obtained by taking the heads of the bands as abscissæ and the molecular weights as ordinates is, allowing for possible slight experimental errors, a straight line.

In the simple equation $y = mx + k$, if for y we substitute M , the molecular weight, and $1/\lambda$ (head of band) for x , this becomes $M = m/\lambda + k$, whence, by substituting numerical values for M and $1/\lambda$, $m = -\frac{2}{3}$, and $k = \frac{2}{3}1/\lambda + M = 2174$ (the mean value).

A close relationship thus evidently exists between the molecular weight and the head of the band in this series of similarly constituted compounds, and doubtless the same holds for other series.

EXPERIMENTAL.

4-Hydroxybenzeneazofornamide (*p*-Benzoquinonesemicarbazone).

This compound was prepared by Thiele and Barlow (*Annalen*, 1898, **302**, 315), who, by acting on a boiling solution of *p*-benzoquinone in alcohol with aqueous semicarbazide hydrochloride, obtained a mixture of the mono- and the di-semicarbazone. Borsche (*Annalen*, 1904, **334**, 175), by working at room temperature, obtained only the mono-derivative. On repeating the preparation as described by Borsche, small quantities of the disemicarbazone were invariably obtained, but on carrying out the operation in ice-cold solutions the formation of the disemicarbazone was wholly avoided.

The colour of the product obtained, even under apparently identical conditions, was found to vary considerably. Sometimes the compound was precipitated in yellow crystals, and at other times a mixture of the yellow with a red variety was obtained.

Yellow Modification.—This is readily obtained pure by dissolving either form in acetone and precipitating by means of light petroleum or carbon disulphide. It may also be prepared from the red modification by rapid crystallisation from hot water. It is thus obtained in tiny yellow needles, melting and decomposing at 165–166°:

0.1506 gave 31.9 c.c. N_2 at 12° and 765 mm. $N = 25.31$.

$C_7H_7O_2N_3$ requires $N = 25.45$ per cent.

Red Modification.—This form is obtained by allowing a hot aqueous solution of the yellow modification to cool slowly or by precipitation of a hot acetone solution by hot benzene. It forms small, red needles, having the same melting point as the yellow isomeride. The change from one form to the other must take place at the melting point, as prolonged heating, even at temperatures near the melting point, causes no change in colour of either form:

0.1580 gave 33.5 c.c. N_2 at 12° and 765 mm. $N = 25.33$.

$C_7H_7O_2N_3$ requires $N = 25.45$ per cent.

Both modifications are equally soluble in water, alcohol, acetone, or glacial acetic acid, giving orange-coloured solutions, and when boiled with dilute sodium hydroxide, yield phenol.

Sodium Salt of 4-Hydroxybenzeneazoformamide,
 $\text{NaO} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CO} \cdot \text{NH}_2.$

This salt is readily prepared by dissolving the parent compound in acetone, adding sodium ethoxide solution in slight excess, and precipitating by means of light petroleum. The salt is purified by dissolving in acetone, filtering off any excess of sodium ethoxide, and reprecipitating with light petroleum. In this way it is obtained in small, red crystals, soluble in water, alcohol, or acetone:

0.3472 gave 0.1304 Na_2SO_4 . $\text{Na} = 12.16$.

$\text{C}_7\text{H}_6\text{O}_2\text{N}_3\text{Na}$ requires $\text{Na} = 12.39$ per cent.

The *silver* salt is obtained as a ruby-red powder by precipitating an aqueous solution of the sodium salt with silver nitrate.

Phenetoleazoformamide, $\text{EtO} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CO} \cdot \text{NH}_2.$

This compound was prepared indirectly by Borsche as described on p. 1406. It has now been prepared directly by heating an acetone solution of 4-hydroxybenzeneazoformamide for several hours on a water-bath under a reflux condenser, with the necessary quantities of dry silver oxide and ethyl iodide. After removing the silver iodide by filtration and distilling off the acetone, the solid residue of the ethyl ether was repeatedly crystallised from methyl alcohol. It is obtained in orange-red leaflets, melting at 162° , soluble in water, alcohol, or acetone, but insoluble in chloroform, or benzene (Found, $\text{N} = 21.89$. $\text{C}_9\text{H}_{11}\text{O}_2\text{N}_3$ requires $\text{N} = 21.76$ per cent.).

4-Acetoxybenzeneazoformamide, $\text{AcO} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{CO} \cdot \text{NH}_2.$

To a solution of 4-hydroxybenzeneazoformamide in absolute alcohol the necessary quantities of sodium, dissolved in alcohol, and acetyl chloride were added. After allowing the mixture to remain for about an hour, the precipitated sodium chloride was removed, and the filtrate allowed to evaporate. From the residue, on crystallisation from alcohol, the acetyl derivative was obtained in long, orange-red needles, melting and decomposing at 158° :

0.1496 gave 26.8 c.c. N_2 at 20° and 756 mm. $\text{N} = 20.38$.

$\text{C}_9\text{H}_9\text{O}_3\text{N}_3$ requires $\text{N} = 20.29$ per cent.

Bromination of 4-Hydroxybenzeneazoformamide: 3:5-Dibromo-4-hydroxybenzeneazoformamide.

This compound was prepared as described by Borsche (*Annalen*, 1904, **334**, 175); it forms yellow needles, melting and decomposing at 223—225°.

The *sodium* salt is obtained in small, red needles by the method already described.

3-Chloro-4-hydroxybenzeneazoformamide,

Seven grams of monochloro-*p*-benzoquinone, prepared according to Levy and Schultz's method (*Annalen*, 1881, **210**, 138, 145), were dissolved in ice-cold alcohol, and mixed with an aqueous solution of 5.5 grams of semicarbazide hydrochloride. The yellowish-brown product which separated was collected, washed with water, and crystallised from acetone with the addition of light petroleum.

The compound is thus obtained in deep yellow crystals, melting and decomposing at 185°. It is soluble in water, alcohol, or acetone, but insoluble in chloroform or benzene:

0.1518 gave 27.4 c.c. N₂ at 17° and 760 mm. N = 20.96.

C₇H₅O₂N₃Cl requires N = 21.05 per cent.

On boiling 3-chloro-4-hydroxybenzeneazoformamide with dilute sodium hydroxide, there is obtained *o*-chlorophenol (b. p. 175°). The decomposition may be represented by the following equation:

From the formation of *o*-chlorophenol it is evident that the semicarbazide attacks the oxygen atom remote from the chlorine.

The *sodium* salt forms dark red crystals:

0.2734 gave 0.0865 Na₂SO₄. Na = 10.25.

C₇H₅O₂N₃ClNa requires Na = 10.38 per cent.

Attempts to prepare a disemicarbazone from chloro-*p*-benzoquinone were unsuccessful.

3 : 5-Dichloro-4-hydroxybenzeneazoformamide,

8.8 Grams of 2 : 6-dichloro-*p*-benzoquinone were dissolved in 200 c.c. of alcohol, and to the well-cooled solution a cold solution of 8.5 grams of semicarbazide hydrochloride in 30 c.c. of water was added. After allowing the mixture to remain in the ice-chest overnight, the orange-red precipitate formed was collected and washed with water. On examining the product with a lens, it was seen to consist of a mixture of red and yellow needles, with the red predominating. The substance was purified by precipitating the acetone solution with light petroleum, when it was obtained in minute, yellow needles, melting and decomposing at 218° :

0.1508 gave 22.5 c.c. N_2 at 15° and 761 mm. $N = 17.79$.

$C_7H_5O_2N_3Cl_2$ requires $N = 17.95$ per cent.

Red Modification.—In attempting to prepare a disemicarbazone of 2 : 6-dichloro-*p*-benzoquinone by the action of excess of semicarbazide hydrochloride, a red precipitate, melting and decomposing at 218° , was formed, which proved to be the isomeric modification of 3 : 5-dichloro-4-hydroxybenzeneazoformamide, and not a disemicarbazone. Attempts to recrystallise this red isomeride as such proved fruitless, the yellow variety being invariably obtained.

Attempts to prepare condensation products of semicarbazide with 2 : 5-dichloro-*p*-benzoquinone, trichloro-*p*-benzoquinone, tetrachloro-*p*-benzoquinone, and chloroanilic acid were all unsuccessful.

4-Hydroxy-*m*-tolueneazoformamide,

This compound was prepared from toluquinone by a method quite similar to that used in the previous preparations. It crystallises from hot alcohol in yellow needles, melting at $178-179^{\circ}$:

0.155 gave 31.1 c.c. N_2 at 16° and 759 mm. $N = 23.38$.

$C_8H_9O_2N_3$ requires $N = 23.46$ per cent.

When boiled with dilute sodium hydroxide, the compound yields *o*-cresol, a reaction which proves that it is the oxygen atom remote from the methyl group that reacts with the semicarbazide base.

The sodium salt forms dark red crystals:

0.3521 gave 0.1227 Na_2SO_4 . $\text{Na} = 11.28$.

$\text{C}_8\text{H}_5\text{O}_2\text{N}_3\text{Na}$ requires $\text{Na} = 11.44$ per cent.

Toluquinonedisemicarbazone,

Two grams of 4-hydroxy-*m*-tolueneazoformamide were dissolved in alcohol, and to the boiling solution an aqueous solution of 1.2 grams of semicarbazide hydrochloride was added, and the mixture heated on the water-bath for an hour. On keeping, an orange-red precipitate separated out; this was collected, washed with water, and dried. The disemicarbazone obtained in this way melts and decomposes at 240° :

0.1218 gave 36.5 c.c. N_2 at 13° and 760 mm. $\text{N} = 35.42$.

$\text{C}_9\text{H}_{12}\text{O}_2\text{N}_6$ requires $\text{N} = 35.59$ per cent.

It is evident from the formation of a disemicarbazone in this way that 4-hydroxy-*m*-tolueneazoformamide acts, like 4-hydroxybenzeneazoformamide, tautomerically, differing in this respect from 3-chloro-4-hydroxybenzeneazoformamide, where the presence of the acidic chlorine atom apparently only allows of the azo-structure.

Bromine Derivatives of 4-Hydroxy-m-tolueneazoformamide:

5-Bromo-4-hydroxy-m-tolueneazoformamide,

Four grams of 4-hydroxy-*m*-tolueneazoformamide, dissolved in 100 c.c. of glacial acetic acid, were mixed with 12 grams of sodium acetate, and a solution of 1 c.c. of bromine in 50 c.c. of glacial acetic acid slowly added. After an hour the mixture was treated with a little water; a yellow precipitate separated, and this was collected and washed with water and alcohol. After repeated crystallisations from boiling alcohol, the monobromo-compound was obtained in yellow needles, melting and decomposing at 205° . It is soluble in water, alcohol, or acetone, but insoluble in benzene, ether, or chloroform; it dissolves in sodium hydroxide solution, yielding a deep red solution of the sodium salt:

0.1394 gave 20 c.c. N_2 at 19° and 755 mm. $\text{N} = 16.39$.

$\text{C}_8\text{H}_5\text{O}_2\text{N}_3\text{Br}$ requires $\text{N} = 16.28$ per cent.

The exact position of the bromine atom in the ring is uncertain,

but by comparison with the analogous compound of known composition obtained by Borsche (*loc. cit.*) on brominating 4-hydroxy-*m*-tolueneazoformanilide, it may be assumed that here also the bromine atom enters the ring in the ortho-position with respect to the hydroxyl group.

Attempts to prepare a pure dibromo-derivative of 4-hydroxy-*m*-tolueneazoformamide were unsuccessful, resulting, as deduced from melting-point determinations and analyses, in mixtures of the monobromo- with higher bromo-derivatives exceedingly difficult to separate. Unfortunately, the quantity of material in our hands did not allow of further investigation.

4-Hydroxy-2-methyl-5-isopropylbenzeneazoformamide,

Eight grams of thymoquinone were dissolved in alcohol, and to the well-cooled solution a cold aqueous solution of 4 grams of semicarbazide hydrochloride was added. After the mixture had remained for some hours in the ice-chest, the yellow precipitate which formed was collected, washed, dried, and crystallised from alcohol. It is thus obtained in bright yellow needles, melting and decomposing at 201—202°:

0.1504 gave 25 c.c. N_2 at 18° and 754 mm. $N=19.04$.

$C_{11}H_{15}O_2N_3$ requires $N=19.0$ per cent.

The sodium salt was obtained in large ruby-red crystals:

0.3552 gave 0.1052 Na_2SO_4 . $Na=9.59$.

$C_{11}H_{14}O_2N_3Na$ requires $Na=9.46$ per cent.

When boiled with dilute sodium hydroxide solution, the compound is completely decomposed with production of thymol, a reaction which indicates its structure.

No disemicarbazone could be obtained from thymoquinone.

Bromination of 4-Hydroxy-2-methyl-5-isopropylbenzeneazoformamide.

3-Bromo-4-hydroxy-2-methyl-5-isopropylbenzeneazoformamide,

This compound was prepared by a method similar to that used in the case of 5-bromo-4-hydroxy-*m*-tolueneazoformamide. After

crystallisation from alcohol, it is obtained in yellow needles, melting and decomposing at 218° . It is soluble in water, alcohol, or acetone, but insoluble in benzene or chloroform :

0.1637 gave 20.4 c.c. N_2 at 21° and 754 mm. $N = 14.07$.

$C_{11}H_{14}O_2N_3Br$ requires $N = 14.0$ per cent.

Preparation of a Dibromo-derivative of 4-Hydroxy-2-methyl-5-isopropylbenzeneazoformamide.

This compound was obtained by acting on the parent substance dissolved in glacial acetic acid with excess of bromine in the presence of sodium acetate. After several recrystallisations from alcohol, it was obtained in small, yellow needles, melting and decomposing at 245° ; it is soluble in water, alcohol, or acetone, but insoluble in benzene or chloroform :

0.1846 gave 18.4 c.c. N_2 at 18° and 744 mm. $N = 11.26$.

$C_{11}H_{13}O_2N_3Br_2$ requires $N = 11.08$ per cent.

In order to elucidate the position of the second bromine atom in the compound, an attempt was made to prepare a hydroxyazo-derivative of dibromothymoquinone, but proved unsuccessful, no reaction taking place. This fact makes it doubtful whether the second bromine atom enters the nucleus or displaces hydrogen in the side-chain.

Attempt to Prepare a Semicarbazone of p-Benzoquinonechloroimide.

As the compounds formed by the action of semicarbazide hydrochloride on *p*-benzoquinone and its derivatives in the proportions necessary for the formation of monosemicarbazones were found to be undoubted azo-compounds, it was considered advisable to attempt to prepare a compound in which a change from a semicarbazone to the isomeric hydroxyazo-structure was excluded. With this end in view, an attempt was made to prepare a semicarbazone of *p*-benzoquinonechloroimide.* By acting on *p*-benzoquinonechloroimide in the usual manner with semicarbazide hydrochloride, a yellow precipitate, evidently of the desired semicarbazone, was immediately formed, but, despite every precaution, decomposed before it could be collected.

Summary.

1. The compounds formed by the interaction of equimolecular proportions of the *p*-quinones and semicarbazide hydrochloride are

* *p*-Benzoquinoneoximesemicarbazone would be suitable, but as Thiele and Barlow (*loc. cit.*) have pointed out that it is insoluble in alcohol or water, it would be impossible to study its absorption spectrum.

not semicarbazones, but hydroxyazo-derivatives. This is proved by their absorption spectra being of the type of those of azobenzene and other typical azo-compounds.

2. Quinonesemicarbazones must, however, in some of the compounds be formed under certain conditions, as is shown by the formation of disemicarbazones.

3. The salts of the hydroxybenzeneazoformamides, on the other hand, possess quinonoid structure, as is proved by their absorption curves being of the same type as that of the undoubted quinonoid compound, tetraphenylquinodimethane.

4. The position isomerides, theoretically possible, cannot be obtained, owing to what is generally accepted as steric hindrance.

5. A direct relationship exists between the molecular weight and positions of the absorption bands in this series of similarly constituted compounds.

In conclusion, we desire to take this opportunity of expressing our indebtedness to Prof. Henderson for the interest he has taken in this work.

CHEMISTRY DEPARTMENT,
ROYAL TECHNICAL COLLEGE, GLASGOW.