AZOXY COMPOUNDS

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## I. THE ISOMERISM AND PROPERTIES OF AZOXYBENZENE

Azoxybenzene was first made by Zinin (1) in 1841 by reducing nitrobenzene with alcoholic potassium hydroxide. It was shown by him to be an intermediate product in the reduction of nitrobenzene to aniline, and was given the formula $C_6H_5N_2OC_6H_5$.

Since its discovery a very large number of derivatives have been prepared and their chemical properties have been studied. Considering the nature of other products of the reduction of nitrobenzene—nitrosobenzene, phenylhydroxylamine, azobenzene and hydrazobenzene—the stable nature of azoxy compounds is remarkable. They are not attacked by dilute nitric, sulfuric, or hydrochloric acid, or by sodium hydroxide solution. They are, in general, resistant to the action of oxidizing agents. They show considerable stability toward many reducing agents. They are not attacked by hydroxylamine or by phenylhydrazine, and many other reagents have no action upon them. They appear, in fact, to be an intermediate stage in the reduction of nitrobenzene derivatives to amines, with an unexpected degree of stability.

Naturally the possibility of isomerism in the case of azoxy compounds has interested many chemists; since a discussion of these compounds is vitally dependent on their structure this topic will first be considered.

The early representation of the molecule of azoxybenzene suggested by Kekulé, indicated two phenyl groups connected

through the agency of a three-membered ring composed of two nitrogen atoms and one oxygen atom as follows:
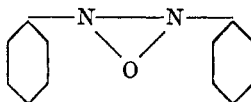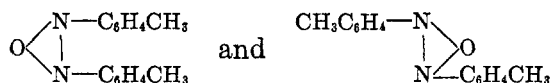

This formula, as is obvious, contains trivalent nitrogen atoms. It had no experimental basis but was arbitrarily selected.

In 1870, Melms (2) succeeded in making p,p'-azoxytoluene, melting at 70°C., by reducing p-nitrotoluene with sodium amalgam in an alcoholic solution. Janovsky and Reimann (3) later reported a second p,p'-azoxytoluene, melting at 75°. The authors considered it to be isomeric with the compound made by Melms, which they called the α form; they called their own compound the β form. The inclusion in Beilstein (3a) of the work of Bamberger and Renauld (4) under the β compound suggests that the Janovsky and Reimann compound was also made by these authors. Reference to the original papers, however, shows the one made by them to have a melting point of 69°. No doubt this compound is identical with that of Melms. Cumming and Ferrier (5) were unable to obtain the isomer melting at 75° by either of the methods used by Janovsky and Reimann, and have further shown that it is not a solid solution of p,p'-azotoluene in p,p'-azoxytoluene. They believed the existence of this β isomeride "extremely doubtful." Further Hantzsch and Werner (6) stated that H. Goldschmidt in a private communication reported that he had not been able to substantiate the claim of Janovsky and Reimann.

The work of Melms had seemed to suggest the possibility of isomerism among azoxy compounds. The same year Kekulé and Hidegh (7) obtained, by the action of phosphorus pentachloride on p-monohydroxyazobenzene, a compound which they believed to be p-monohydroxyazoxybenzene. These investigators gave no melting point, but the work of Wallach and Kiepenheimer (8) established it as 145°. The fact that the compound formed p-monohydroxyazobenzene on treatment with alcohol and sodium seemed to support the view of Kekulé and Hidegh regarding its

constitution, but its insolubility in alkalies and its failure to react with acetic anhydride even at 180° to 200° denied this probability. Later Bamberger (9) prepared a p-monohydroxyazoxybenzene by condensation of p-nitrosophenol and phenylhydroxylamine and found it to melt at 156.5°. Later still Angeli prepared both the α and β isomers of this compound: the α isomer had a melting point of 156° and was identical with the compound prepared by Bamberger; the β isomer had a melting point of 117°. The compound which Kekulé and Jidegh prepared is not identical with either of these and cannot be considered as an isomeric p-monohydroxyazoxybenzene. So far as we have been able to find, no further investigation of this compound has been made.

Up to 1890, then, only one case of apparent isomerism was known, namely, that of p,p'-azoxytoluene. Early in that year Hantzsch and Werner (10), in an extended consideration of the isomerism of nitrogen compounds, suggested that azoxy compounds might illustrate stereoisomerism of the geometric type, quite closely analogous to the suggested isomerism of the azo compounds. Between the nitrogen atoms there might be considered to be two bonds, one of them through an intermediate oxygen atom. They represented the two isomeric p,p'-azoxytoluenes by the formulas

$$O\Big\langle{\overset{N-C_6H_4CH_3}{\underset{N-C_6H_4CH_3}{|}}} \quad \text{and} \quad {\overset{CH_3C_6H_4-N}{\underset{N-C_6H_4CH_3}{|}}}\Big\rangle O$$
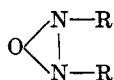
The authors suggested the formulas with little comment. They did not suggest, as was later pertinently pointed out by Angeli, that such isomers, if of the usual type, should be capable of transformation one into the other through the agency of heat, bromine, acid, etc.
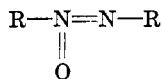
In 1900 Bamberger, through the action of aqueous sodium hydroxide on nitrosobenzene (11) and later (12) by the action of light on a benzene solution of nitrosobenzene, found what he at first considered as two o-monohydroxyazoxybenzenes. One melted at 75.5°–76°; the other, which he called iso-o-hydroxyazoxybenzene, melted at 108°–108.5°. He came to the conclu-

sion (9) that only one was an azoxy compound, the other being orthoquinoid in character. Later, however, he suggested that they might possibly be *cis* and *trans* isomers (13). This is particularly interesting, for later Bigiavi and Poggi (14) established the fact that both of these were azoxy compounds and isomeric with one another.

In 1901 Wacker (15) made α-azoxynaphthalene by the reduction of α-nitronaphthalene with ammonium chloride and zinc dust, and from α-nitronaphthylhydroxylamine. He found two products: one was yellow and melted at 127°; the other was red and melted at 126.5°. Both belonged to the rhombic system. He noticed further that light turned the yellow compound into the red one. He considered both to be α-azoxynaphthalenes. Here then we have what may possibly be considered a case of geometrical isomerism. Cumming and Steel (16) in 1923 reported the formation of two azoxynaphthalenes from α-nitronaphthalene dissolved in alcohol to which ammonium chloride was added, followed by the gradual addition of zinc dust. They found both the yellow and red modifications of Wacker; both melted at 127°. The yellow form became red in the sunlight. They believed the change from the yellow to the red modification to be represented by a change of structure
from

$$O\!\!\left\langle\begin{array}{l} N\!-\!R \\ | \\ N\!-\!R \end{array}\right.$$

to

$$\begin{array}{c} R\!-\!N\!=\!\!N\!-\!R \\ \| \\ O \end{array}$$

The absorption coefficients showed that the two forms were not dimorphous. It should be remarked, however, that Baudisch and Fürst (17) have studied the action of light on α-azoxynaphthalene and have shown that α-naphthaleneazo-α-naphthol, melting at 224°, is formed. Furthermore, in a later communication, Cumming and Ferrier (18) in a study of the action of light on

azoxy compounds reported a private communication from Cumming and Steel stating that the latter had found that, on long exposure to light, α-azoxynaphthalene gives the α-naphthalene-azo-α-naphthol, melting at 224°, found by Baudisch and Fürst. It is possible, then, that they mistook a transformation into a hydroxyazo compound for a stereoisomeric change.

In 1909 Reissert (19) undertook a further study of azoxy compounds with the possibility of stereoisomerism in view. He assumed that compounds made at an elevated temperature would give only the isomer stable at that temperature, while at a lower temperature he might get pairs of such isomers. With this in view he used a water alcohol solution of sodium hydroxide on nitrosobenzene, the mixture being ice-cooled. He obtained ordinary azoxybenzene melting at 36° and, in small quantities, an isomeric form melting at 84°. By condensation of phenylhydroxylamine with nitrosobenzene under similar conditions he got no trace of the new isomer. With o-nitrosotoluene, reduced as above, he got the usual o-azoxytoluene, melting at 59–60°, and an isomeric isoazoxytoluene melting at 82°. With the corresponding *para* compound he got only the usual *p*-azoxytoluene melting at 70°.

These iso isomers, in both cases, according to Reissert, go gradually into the better known isomers with increase of temperature. He found no fixed transition point; however, the higher the temperature the higher the rate of transition.

Angeli (20) reported that he had been unable to corroborate the work of Reissert in the preparation of isomers of azoxybenzene at low temperatures. His method, however, was not a duplication of that of Reissert's, but consisted in the oxidation of azobenzene with peracetic acid. Nevertheless one might reasonably expect that, if the condition governing the formation of the two isomers is that of definite temperature, the isomers might be expected, whatever the method of preparation.

The work of Reissert, however, is another case in which there is evidence of stereoisomerism of the geometrical type. Still another case has recently been observed by Cumming and Ferrier (21). These experimenters prepared β,β'-azoxynaphthalene by

reducing β-nitrosonaphthalene with zinc dust and ammonium chloride in alcohol. Their product melted at 164°. Meisenheimer and Witte (22) gave a melting point of 167–168°. Cumming and Ferrier exposed their compound to light and obtained a red compound melting at 162°; this change is irreversible. In view of the fact that Knipscheer (23) has shown that azoxybenzene is converted by light into o-hydroxyazobenzene and Baudisch and Fürst (17) have shown that α-azoxynaphthalene is changed into α-naphthaleneazo-α-naphthol, the authors tried to show the presence of a hydroxyl group in their compound by benzoylation and methylation, but failed. Support for the assumption of its presence is given, however, by a comparison of the absorption spectra of both their yellow and red isomers with that of β-naphthaleneazo-β-naphthol. Both the red isomer and the β-naphthaleneazo-β-naphthol produced a band with its head at a frequency approximately 1950 units, which was not shown by the yellow isomer; and, furthermore, the characteristic absorption bands of the yellow isomer were not shown by the red. It would, then, seem doubtful that two isomeric azoxy compounds are here described. The color of the red isomer is noteworthy. Azoxy compounds are not deeply colored; they vary, in general, from pale yellow to golden. What structural change due to stereoisomerism could cause such a change in color is not clear. The formation of an azo compound by the action of light gives a perfectly satisfactory explanation of the color change.

We have grouped together the various examples of isomers, which are found in the literature, whose isomerism might be other than structural. There is an element of doubt about the existence of most of them. Probably all of them should be studied further, but most particularly those obtained by Reissert. This author's work should be repeated with care.

There still remains the possibility of structural isomerism, and it is this field which has proved so productive in recent years in the study of the structure of azoxy compounds. Its development is due to Angelo Angeli of the University of Florence, Italy, and to his students. According to his view no isomerism is to be expected in the case of symmetrical compounds of the type of

azoxybenzene (fig. 1) but with a compound like benzeneazoxy-*p*-nitrobenzene two isomers might be expected if the oxygen atom is attached to one nitrogen only, it being pentavalent. They would differ according as the single substituting group were in the ring adjacent to the trivalent or to the pentavalent nitrogen. Whether geometrical isomerism may occur or not there can be no doubt of the existence of structural isomers among the azoxy compounds when they are unsymmetrical. That such isomers were not early observed was due to the methods by which azoxy compounds were made. Such methods consisted in the reduction

Azoxybenzene

α Isomer
m.p. 152°

β Isomer
m.p. 148°

Benzeneazoxy-*p*-nitrobenzene (or *p*-nitroazoxybenzene[1])
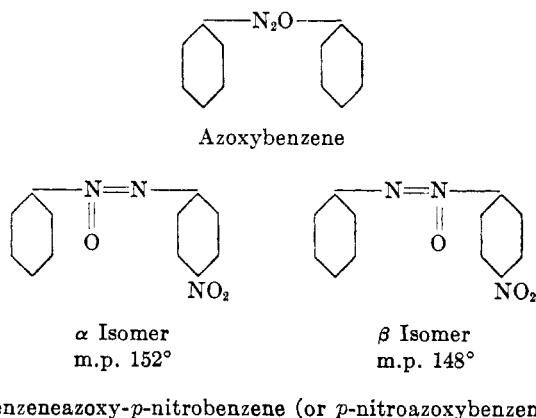
Fig. 1. Azoxybenzene and Isomers of Benzeneazoxy-*p*-nitrobenzene

of compounds containing a nitro group and, of necessity, led to symmetrical compounds.

The genesis of Angeli's representation of the isomerism of azoxy compounds is probably found in the discussion of the structure of the so-called nitrosophenylhydroxylamine discovered by A. Wohl (24) and a little later by E. Bamberger (25). Both of these investigators prepared it by the action of nitrous acid on phenylhydroxylamine and both gave to it the formula,

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[1] Two systems of nomenclature of azoxy compounds are found in the literature. In figure 1 the two isomeric nitro substituted azoxybenzenes are called α and β *p*-nitroazoxybenzene. They are also called α and β benzeneazoxy-*p*-nitrobenzene. We prefer the latter system, though the former is more common. We have used both systems in this paper, largely dependent on their use by the author whose work is being discussed.

$$C_6H_5N\diagdown{}^{NO}_{OH}$$
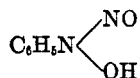
In 1896 Angeli (26) published a new method for the preparation of this interesting substance by condensing nitrobenzene with hydroxylamine and, from its method of preparation, gave it the formula

$$C_6H_5N{=}N{-}OH$$
$$\|$$
$$O$$
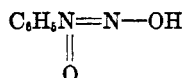
This compound, melting at 58.5°, is identical in all respects with that prepared by Wohl and Bamberger and is isomeric with diazobenzolic acid, melting at 46°. There has been a great deal of discussion concerning the structure of these two compounds which it is not necessary to detail. It is of interest here as the probable source of the idea that azoxy compounds of dissimilar aryl groups might be expected to exhibit isomerism if connected by the grouping.

$$-N{=}N-$$
$$\|$$
$$O$$
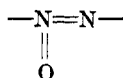
Later in the same year Bamberger and Ekecrantz, in a discussion of the compound formed by the methylation of nitrosophenylhydroxylamine, suggested that its formula might be

$$C_6H_5{-}N\text{------}N{-}OCH_3$$
$$\diagdown\diagup$$
$$O$$
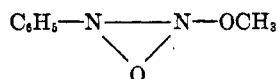
and in a footnote stated that it is purely arbitrary whether the N_2O group be represented as in the above formula or by the symbol

$$-N{=}N-$$
$$\|$$
$$O$$
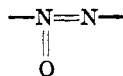
and that the same is true for azoxybenzene. On the strength of this note some would give to Bamberger the credit for the suggestion of this structure for azoxybenzene (19). This would hardly seem justified in view of Angeli's work some months earlier. Indeed, the application of this formula to azoxy compounds

had hardly been thought worthy of consideration by Bamberger, since four years later, though he was the first to discover two thoroughly authentic isomeric azoxy c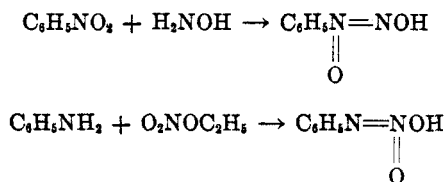ompounds—the two benzene-azoxy-o-phenols—he did not see in them confirmation of this theory of the structure of azoxy compounds but gave to one the quinoid formula.

During the following ten years many azoxy compounds were made, all of them symmetrical in type. In 1906 Angeli and Marchetti (27) studied the reaction of sodium on a mixture of nitrobenzene and aniline. They obtained a compound containing sodium which was readily hydrolyzed yielding an appreciable quantity of azoxybenzene. Similarly, the condensation of α-naphthylamine and α-nitronaphthalene in the presence of sodium gave α-azoxynaphthalene. When, however, they condensed in this way aniline and α-nitronaphthalene, or nitrobenzene and α-naphthylamine, they obtained two isomeric compounds probably represented by the formulas

$$C_6H_5N\!\!=\!\!NC_{10}H_7 \qquad and \qquad C_6H_5N\!\!=\!\!NC_{10}H_7$$
$$\underset{O}{\overset{\|}{}} \qquad\qquad\qquad \underset{O}{\overset{\|}{}}$$
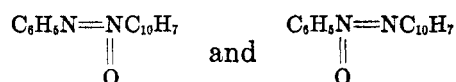
The condensation of amines with nitro derivatives in the presence of sodium they considered as general in character. Among others they gave methods for the preparation of the isomeric compounds nitrosophenylhydroxylamine and diazobenzolic acid as follows:

$$C_6H_5NO_2 + H_2NOH \rightarrow C_6H_5N\!\!=\!\!NOH$$
$$\underset{O}{\overset{\|}{}}$$

$$C_6H_5NH_2 + O_2NOC_2H_5 \rightarrow C_6H_5N\!\!=\!\!NOH$$
$$\underset{O}{\overset{\|}{}}$$

It would seem then that the possibility of structural isomerism among azoxy compounds was established in the mind of Angeli at that time. The difficulty of preparing such compounds, however, was great. The condensation of aniline with nitrobenzene does not take place readily. Various attempts to condense the

two substance had been made with condensing agents other than
sodium but without success.   Another method had to be found if
a real advance were to be made.   The promising method of
Bamberger (28)—the condensation of nitrosobenzene and a sub-
stituted phenylhydroxylamine—did not give results.   Instead,
two symmetrical compounds were formed as follows:

$$C_6H_5NO + p\text{-}BrC_6H_4NHOH \rightarrow BrC_6H_4N_2OC_6H_4Br + C_6H_5N_2OC_6H_5$$

As a consequence Angeli sought to oxidize unsymmetrical azo
compounds.   H. Petriew (29) had obtained trinitroazoxytoluene
by treating azotoluene with strong nitric acid, the azo group being
oxidized but the ring attacked as well.   Azobenzene, too, treated
with an acetic acid solution of chromic acid in an enclosed tube at
150° to 250° gave azoxybenzene.   It was, however, found later
by Angeli that this reagent had occasionally the power of trans-
forming an azoxy compound into its isomer.   These facts made
both of these reagents undesirable as oxidizing agents for the azo
group alone.   Angeli (30) therefore studied the action of perace-
tic acid—made by combining glacial acetic acid with 30 per cent
hydrogen peroxide—on azobenzene and found that, on standing
for several days, azoxybenzene was obtained.   It is this reaction
between peracetic acid and azo compounds which has made pos-
sible the extended study of azoxy compounds since 1910.

The first work was done by Angeli and Alessandri (31) on p-
nitroazobenzene.   Treating this with peracetic acid they ob-
tained two isomeric forms: one, that obtained by Zinin (32),
melted at 152°; the other had a melting point of 148°, which later
(33) was given as 149°.   They suggested that these are structural
isomerides; since one of them—that with melting point 152°—is
the older and formed by the action of nitric acid on azoxybenzene
it should be called the α form; the other was called the β form.
These isomers with their melting points are shown in figure 2;
the differences in their constitution are not shown.

Shortly after, Angeli and Valori (34), by oxidizing p-bromoazo-
benzene with hydrogen peroxide and glacial acetic acid, obtained
two isomeric compounds, one melting at 73°, the other at 92°.
They are shown in figure 2 without constitutional differences.

The former is identical with that made by treating azoxybenzene with bromine and is called the α form. Neither of the pairs shown in figure 2 can be transformed, the one into the other, by the usual methods effective with stereoisomers of the geometrical type. They are, however, both reduced to the same azo compound.

To determine the particular structure of each of these pairs it was necessary to consider their chemical action toward various reagents. Both of the α forms were unaffected by nitric acid of

α Forms β Forms

m.p. 152°   m.p. 148°

p-Nitroazoxybenzene

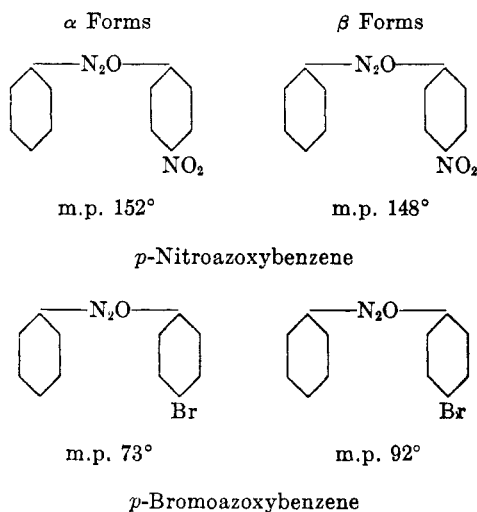m.p. 73°   m.p. 92°

p-Bromoazoxybenzene

FIG. 2. ISOMERIC FORMS OF p-NITROAZOXYBENZENE AND p-BROMOAZOXYBENZENE

specific gravity 1.45, but both the β forms were nitrated forming respectively p,p'-dinitroazoxybenzene and p-bromo-p'-nitroazoxybenzene. So, also, treated with bromine, the α forms were unattacked, but the β forms gave p-bromo-p'-nitroazoxybenzene and p,p'-dibromoazoxybenzene, respectively. This action is expressed in figure 3.

In the formula of azoxy compounds suggested by Angeli one of the nitrogens is trivalent, the other pentavalent. To determine the position of each of these, Angeli compared the action of nitric acid and of bromine on azo compounds. p-Bromoazobenzene

acted on by bromine gave p,p'-dibromoazobenzene and with nitric acid it gave p-bromo-p'-nitroazobenzene; in both cases the unsubstituted ring was attacked. So also p-nitroazobenzene with bromine gave p,p'-bromonitroazobenzene and with nitric acid it gave p,p'-dinitroazobenzene. In the case of both com-
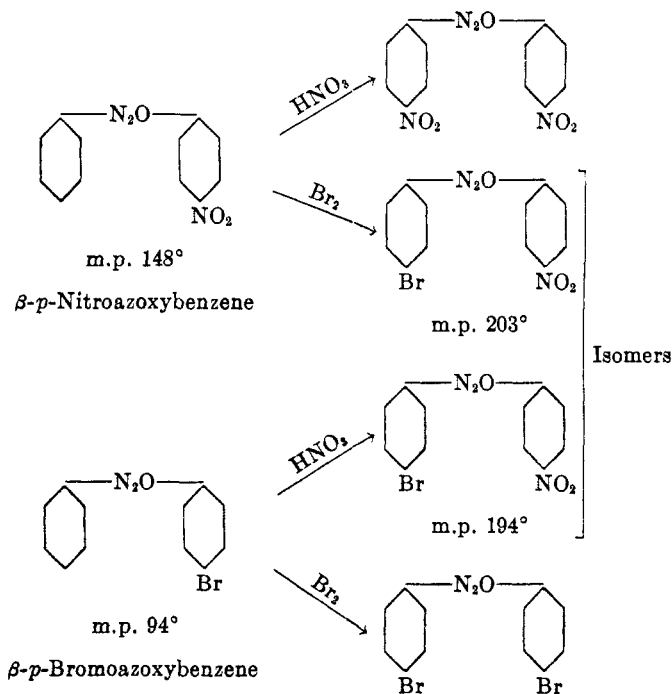

FIG. 3. ACTION OF NITRIC ACID AND OF BROMINE ON THE β FORMS OF p-NITRO-AZOXYBENZENE AND OF p-BROMOAZOXYBENZENE

pounds treated with bromine or nitric acid substitution occurred in both rings as shown in figure 4.

In all these cases the bromo or nitro group entered a ring *para* to a trivalent nitrogen. Many other examples could be given to illustrate this fact. It would seem, therefore, a fair assumption that when a single bromo or nitro group enters the ring of an azoxy compound it does so in a ring which is bound to a trivalent nitrogen atom.

On this assumption the well known benzeneazoxy-*p*-nitroben-zene, more commonly called *p*-nitroazoxybenzene, and which Angeli calls the α isomer, must have its nitro group in the ring attached to a trivalent nitrogen, and the oxygen attached to the pentavalent nitrogen must be adjacent to the second ring; so
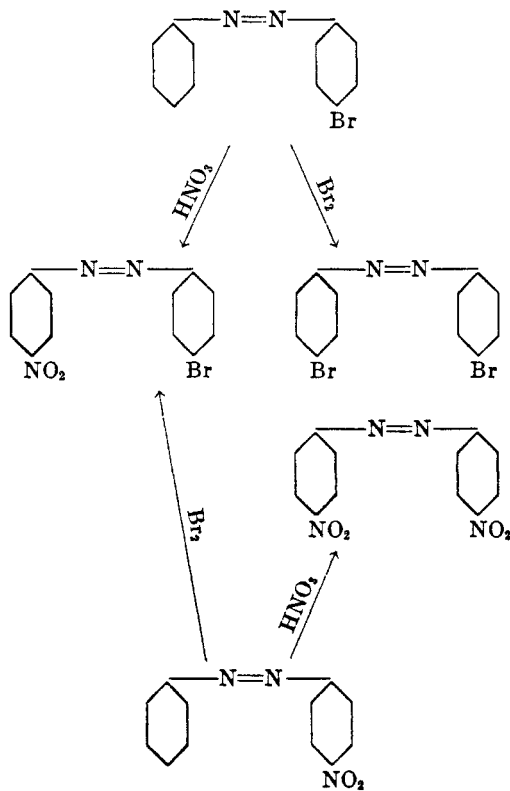

FIG. 4. ACTION OF BROMINE AND OF NITRIC ACID ON *p*-BROMOAZOBENZENE AND ON *p*-NITROAZOBENZENE

with others which contain a single substituting group. On that assumption we can represent the structural formulas of the various isomers in figures 2 and 3 which contain bromo and nitro-groups as shown in figure 5.

The two *p*-bromo-*p'*-nitroazoxybenzenes in figure 5 were pre-

pared in 1912 by Angeli and Valori (34). *α-p*-Bromo-*p'*-nitro-azoxybenzene, m.p. 194°, was obtained by oxidizing *p*-bromo-*p'*-nitroazobenzene with peracetic acid. It is noteworthy that only one of the isomers was obtained. The other, *β-p*-bromo-*p'*-nitroazoxybenzene, was prepared from *β-p*-nitroazoxybenzene with bromine and a trace of iodine as a carrier. Its melting

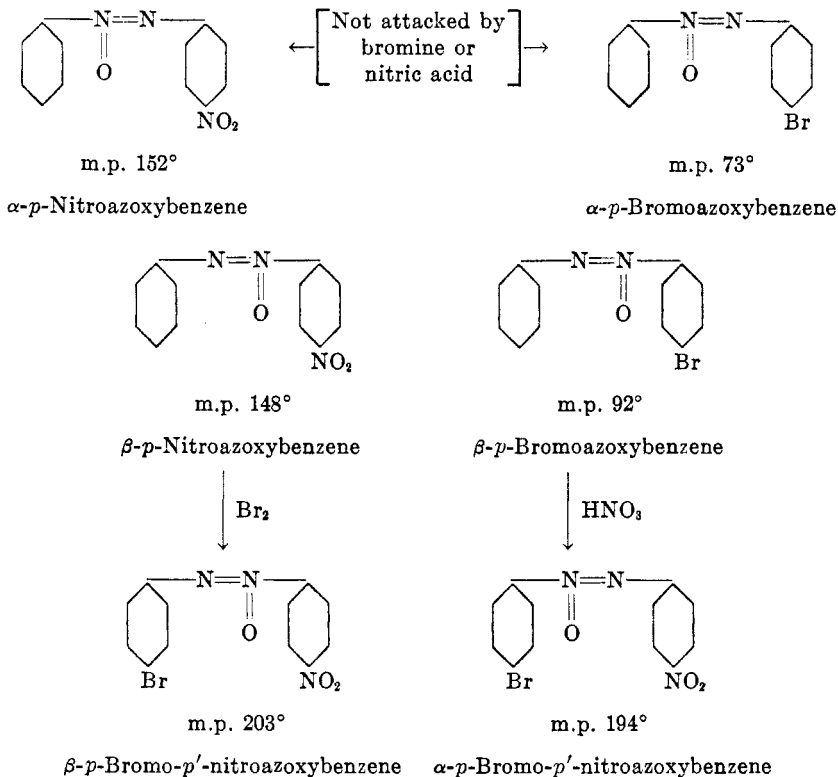Fig. 5. Structure of Isomers of Bromo and Nitro Derivatives of Azoxybenzene

point is 203°. Angeli and Alessandri (33) gave 199° as its melting point when made in the same way.

Other azoxy isomers that have been studied are the benzene-azoxy-*p*-phenols. It will be remembered that one of these, that with melting point 156°, was prepared by Bamberger (9) by the condensation of *p*-nitrosophenol and phenylhydroxylamine.

In 1914 Angeli (35) heated the acetyl derivative of benzeneazo-*p*-phenol with hydrogen peroxide and acetic acid and saponified the product. From it he obtained two benzeneazoxy-*p*-phenols, one with melting point 156°, identical with that of Bamberger, and another with melting point 107°. In a later research (36) he dealt with the constitution of these isomerides. They were found to be most easily separated by means of their benzoyl derivatives. When that of the isomer with melting point 107° was hydrolyzed it gave a compound with melting point 117°, showing that the value 107° found earlier was incorrect. Valori (37) shortly after
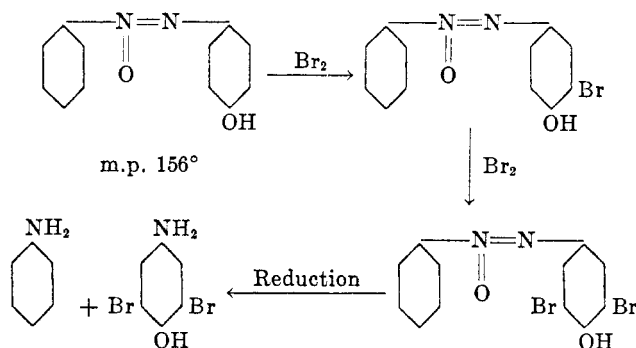

FIG. 6. CHANGES BROUGHT ABOUT BY BROMINATION OF α-BENZENEAZOXY-*p*-PHENOL AND REDUCTION OF THE PRODUCT

found it to be 117°, in agreement with Angeli's later value. Bigiavi and Sabatelli (38) in 1927 found it to be 118°. Angeli (36) suggested that of these two benzeneazoxy-*p*-phenols, that discovered by Bamberger and melting at 156°, should be given the α structure. In support of this view he brominated it, whereby a monobromo derivative was formed and later a dibromo derivative was obtained. A tribromo derivative could not be made by bromination. The dibromo derivative on reduction with zinc and acetic acid gave 2,6-dibromo-4-aminophenol, aniline and benzanilide. Since it is postulated that bromine enters the ring attached to a trivalent nitrogen and is, in fact, found in the ring containing the hydroxyl group, the conclusion follows that the hydroxyl group must be in this ring also. This establishes the

structure of the original benzeneazoxy-*p*-phenol as an α-compound. The relationship is shown in figure 6.   It is interesting to report that a tribromo derivative of this compound could be obtained only by bromination of α-bromobenzeneazoxy-*p*-phenol as follows:
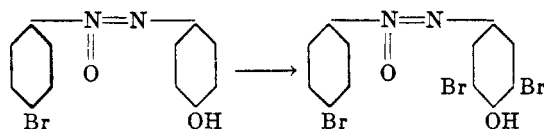
To the benzeneazoxy-*p*-phenol, *m.p.* 117°, must be given the β form.   Figure 7 will illustrate this relationship and that of some of the derivatives of these compounds.   Further, Valori (37) treated the ethyl ether of α-benzeneazoxy-*p*-phenol, *m.p.* 72°, with nitric acid and obtained benzeneazoxy-*m*-nitro-*p*-ethoxybenzene, in this way further establishing the position of the trivalent nitrogen in the azoxy group.   Thus considerable evidence has been adduced as to the structure of the two benzeneazoxy-*p*-phenols as given in figure 7.

Still another pair of isomers illustrates this phenomenon of isomerism.   Bigiavi and Sabatelli (38) oxidized benzeneazo-*p*-toluene with peracetic acid and obtained two benzeneazoxy-*p*-toluenes.   The α isomer
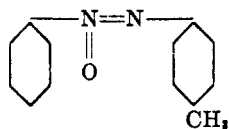
melts at 46°, the β isomer
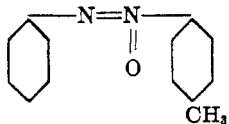
obtained in smaller quantities melts at 65°.   The former was accepted as the α compound since it did not react with bromine. The latter gave a *p*-bromo derivative and was therefore the β compound.   Its constitution was established by reduction with

tin and hydrochloric acid to form p-bromoaniline and p-toluidine; and by reduction with aluminium amalgam to a hydrazo compound not isolated which, oxidized with mercuric oxide, gave p-bromobenzeneazo-p-toluene with a melting point of 153°, identical with that obtaimed from p-bromo aniline and nitrosotoluene by condensation. The β isomer, then, is the one containing the unsubstituted ring attached to a trivalent nitrogen. Fur-
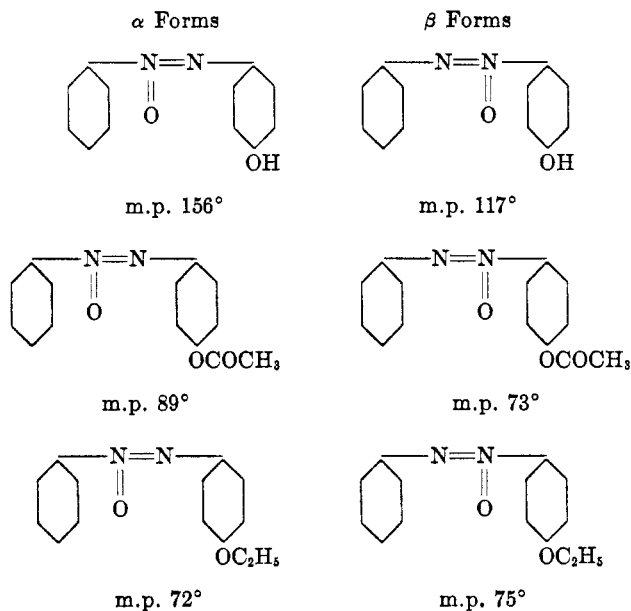
FIG. 7. α AND β FORMS OF BENZENEAZOXY-p-PHENOL AND SOME OF ITS DERIVATIVES

ther the β compound gave a p-nitro derivative, with melting point 163°, identical with the product obtained by the action of peracetic acid on p-nitrobenzeneazo-p-toluene.

The foregoing illustrations are well established examples of structural isomerism among azoxy compounds and constitute adequate experimental evidence of the existence of such isomers. The fundamental assumption on which their structure is based is that the oxygen of the azoxy group is attached to a pentavalent

nitrogen, the second nitrogen being trivalent as in azo compounds. In these latter compounds both bromine and nitric acid cause substitution in both rings; with the azoxy compounds in one ring only. The conclusion seems justified that the oxygen of the azoxy group exerts a protective action on the ring to which it is adjacent. On this assumption the isomers are classed as α or β. Further, such protective effect is not confined to the action of nitric acid and bromine only. In the case of the two benzene azoxy-p-toluenes already given (38) the α isomer is readily oxidized by chromic acid to the corresponding benzeneazoxy-p-benzoic acid, melting at 231°, while the β isomer is only slowly transformed into the corresponding compound melting at 241°. So great is the difference in the speed of the reactions that the β compound may be recovered in a pure condition after a mixture of the two is treated with chromic acid. A similar difference is observed in the case of the α and β hydroxy substituted benzenes as will be shown later.

II. MOLECULAR REFRACTION OF AZOXY COMPOUNDS

Further information concerning the structure of azoxy compounds has been adduced from a study of their absorption spectra, their molecular refractivity and diffraction, and from their molecular volumes.

Many investigators have studied the refractive power of both elements and compounds toward light of various wave lengths and, with a considerable degree of success, have been able to show a relationship between the structure of organic compounds and their molecular refractivity. The values to be ascribed to the atoms—the atomic refractivity—have been calculated from the data for molecular refractivity and in this way, also, the values for various groups and linkages have been determined. Bruhl, a distinguished investigator in this field, has carried out an extended series of investigations on organic nitrogen compounds. In two of his papers (39) he determined the constants for azoxybenzene and concluded that they are irreconcilable with the three-ring formula. He suggests that a diazonium-like structure would best represent it and that either

$$C_6H_5N{=}NC_6H_5 \quad\text{or}\quad C_6H_5N{\equiv}NC_6H_5$$
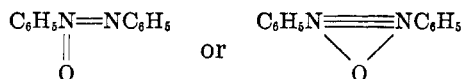
would represent the true structure, though he could not discriminate between them. No further study of the spectro-chemical behavior of azoxy compounds was made until 1928 when Auwers and Heimke (40) undertook a more extended investigation of these compounds. Auwers (41) had pointed out earlier that a three-membered carbon ring has a constant refractive increment and that the system A (figure 8) in ethylene oxide and related compounds is optically normal. The same is true for the three-membered system ethyleneimine B (figure 8) and its homologues, as pointed out by Markwald and Frobenius (42). Auwers (41) has further shown that the ring C (figure 8) in the dimethyl and diethyl esters of hydrazoisobutyric acid exerts no exalting
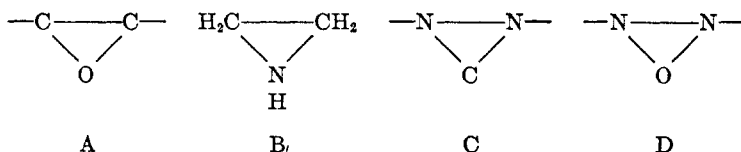
FIG. 8. CERTAIN THREE-MEMBERED RINGS

influence but, on the contrary, diminishes the molecular refractivity. Auwers and Heimke (43) conclude from these facts that there is no probability of the ring D (figure 8) increasing the molecular refractivity of a molecule. It is, however, a general characteristic of azoxy compounds that their molecular refractivities are high—always higher than that calculated from the atomic refractivities. These compounds, if of the ring structure, should give values for $E\Sigma_D^{20}$ approximately equal to that of hydrazobenzene and its derivatives. For these, however, this value is about 1.35, almost a complete unit below that of azoxybenzene.

Further, Auwers and Heimke examined the α and β forms of various azoxy compounds and found the differences in molecular refraction between them to be very small. They concluded that their isomerism is not due to a difference of structure like that between the old and the new formulation. Indeed they further

noted that recent research has more and more destroyed belief in three-membered rings. They however drew attention to the fact of their own experience that o,o'-azoxytoluene shows spectrochemical constants extraordinarily low. Further study is necessary for the explanation of this.

III. ABSORPTION SPECTRA

Studies in this field, particularly those of Hartley, have shown that substances of closely allied structure have absorption curves of similar form. By a comparison, then, of the absorption curve of a substance of unknown constitution with that of a known and related compound, valuable evidence regarding its structure may be obtained. If the molecular absorption curves for the two are similar, similarity of constitution may be assumed. There is much experimental evidence to support this conclusion. Absorption curves are plotted with frequency or wave length in Ångström units as abscissae and the log of molecular absorption as ordinates.

Szego (44) has studied the absorption spectra of a number of azoxy compounds in the ultra-violet part of the spectrum and has found that the curves for the isomeric α- and β-p-monobromoazoxybenzenes and the similar pair of nitro isomers are very similar, but with the hydroxy substituted product, and with the p,p'-bromonitroazoxybenzene considerable differences are found. This is all the more noteworthy in the latter case since the entrance of halogen and of nitro groups as substituents in the ring is generally without influence on the optical activity of compounds, as shown by Auwers (45). In general, however, Szego concluded that the results run parallel with the behavior of the two isomers as expected from their formulas as suggested by Angeli. All α forms show, besides the characteristic maximum for all azoxy compounds, a second band in the neighborhood of 2600 to 2500 Ångström units which the β forms lack. With α-2-methyl-5-hydroxyazoxybenzene three maxima are found compared with one in the β compound.

Szego (46) further carried out a comparison of the absorption curves of α and β isomers with that of the corresponding azo

compound. He found that the transformation of monobromo- and mononitro-azobenzenes into the corresponding azoxy compounds, by the entrance of oxygen, caused either no change in the frequency of the band or a very small one. The bands in the azo compounds were, in general, somewhat more sharply marked and narrower. In the case of hydroxy substituted compounds, however, there is not so great a similarity. The α azoxy compound and the similar azo body showed very similar curves with two maxima, but the β had only one, or a second small one. He suggested that, in the latter compound, the nearness of the hydroxyl or amino group to the "active" oxygen of the azoxy group may account for this irregularity. He also thought it quite possible that there may be a second band in the α compound at a frequency not yet examined. With symmetrically disubstituted derivatives he found close agreement with the azo compound and, in general, a slight displacement of the band toward the red from azo to azoxy, with a more strongly marked band in the azoxy compounds.

The similarity of the absorption curves of azoxy compounds to those of the azo compounds suggests a similarity of structure. To be of greatest value, however, it would be desirable to know what influence, if any, three-membered rings containing nitrogen have on absorption curves. It would seem that further work is necessary before definite conclusions regarding the structure of azoxy compounds can be arrived at from a study of absorption spectra.

IV. PARACHOR OF AZOXY COMPOUNDS

Sugden's device (47) for comparing molecular volumes by the use of a new constant called the "parachor" has excited much interest and prompted considerable research. Through its agency he has been able to determine atomic and structural constants and from them to predict with considerable accuracy the experimental values for a very large number of compounds. Sugden's earlier work gave to the double bond between two atoms the value of 23.2. In a considerable number of cases double bonds showed a value of -1.6. Compounds with double bonds show-

ing this value all belong to the class in which the octet valence theory of Lewis (48) and Langmuir (49) leads to a modification of the usual structural formulas in which a valency bond is written for each pair of shared electrons. This double bond, the so-called "semi-polar" double bond, has been found, according to Sugden (50), to be present in azoxy compounds.

From a study of the parachors of azoxybenzene the value for the group N_2O is calculated to be 64.7. From a study of the parachors of o-azoxytoluene the value is found to be 70.6, clearly not a good agreement. Below are given the calculated values for the group N_2O when represented in the three forms given:

—N———N—	—N=N—	—N=N—
\\ /	‖	‖
O	O	O
62	91.2	66.7
(1)	(2)	(3)
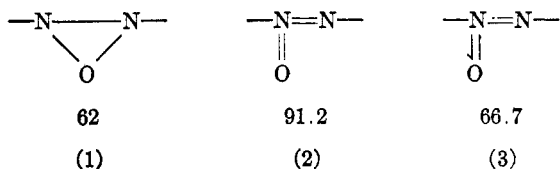
The values as found by Sugden above would exclude form 2, that of Angeli, but would not distinguish between forms 1 and 3. The latter contains, as the octet theory would require, a semi-polar double bond as found in nitrobenzene. Sugden concluded from electrochemical considerations and the fact that azoxy compounds are readily formed by oxidation of azocompounds, that form (3) represents the true linkage between the nitrogen and oxygen. This formula, of course, would in no way invalidate Angeli's explanation of the isomerism of azoxy compounds.

More recent work by Mumford and Phillips (51) showed a closer agreement between the observed and calculated values of the parachor for azoxy compounds. Using the newer values (52) found for the double bond between two nitrogen atoms and for nitrogen itself, and introducing the value for "strain constants" (53), the calculated value for the parachor for azoxybenzene became 447.5 and for o-azoxytoluene 527.5, compared with 444.7 and 528.6 found experimentally by Sugden, Reid and Wilkins (54). These values strongly favor form 3 rather than the three-membered ring or the further form

$$-N \rightleftharpoons N-$$
$$\overset{||}{O}$$
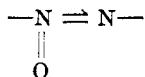
suggested as a possibility by Mumford and Phillips (53), which gives a calculated value for azoxybenzene of 454 and for o-azoxytoluene of 534.0.

We may therefore conclude that the limited number of determined values for the parachors of azoxy compounds favors the formula suggested by Angeli for these compounds, modified by the introduction of the semi-polar double bond required by the octet theory.

V. WALLACH'S TRANSFORMATION

The well-known conversion of azoxybenzene into p-hydroxy-azobenzene by the action of concentrated sulfuric acid was discovered by Wallach and Belli (55) and bears the name of the first of these authors. It is probably of very wide application and has been used to indicate the presence of an azoxy group. The general method is to heat the azoxy compound with the acid and pour the product into water, whereby there is obtained a colored compound soluble in alkali. Despite the simplicity of the method it seems not to have been studied as extensively as might be expected. The simple compound p-mononitroazoxy-benzene has apparently not been treated in this way until recently. Bigelow and Linton (56) have found that this compound, if heated for a short time with concentrated sulfuric acid, gives an almost quantitative yield of p,p'-nitrohydroxyazobenzene and in a nearly pure condition. This compound was prepared originally by condensing p-nitrosophenol with p-nitroaniline, a process by no means simple. Nor has there been until recently a study of the effect of temperature upon the reaction which in the case studied, to be described later under bisazoxybenzenes, greatly modified the course of the reaction.

One might expect that, along with the *para* transformation one would find some of the *ortho* compound formed as well. Bamberger (57) has shown that in the treatment of azoxybenzene with sulfuric acid a small amount of this isomer is actually formed.

The same author (58) explains Wallach's transformation as follows:

$$C_6H_5N{=\!=}NC_6H_5$$
$$\downarrow$$
$$C_6H_5N{=\!=}N{=\!=}C_6H_4\big\langle$$
$$\mid$$
$$OH$$
$$\downarrow$$
$$C_6H_5N{=\!=}NC_6H_4OH$$
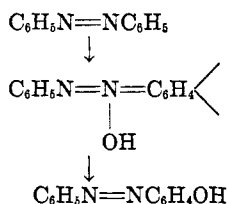
in agreement with the hypothesis of Stieglitz (59). Here the transformation is due to the detachment and migration of a hydrogen atom with resulting free valence which effects the transposition.

Knipscheer (60) has found that at 200° p- and o-hydroxyazobenzenes are obtained by heating azoxybenzene with sulfuric acid, and on heating it with acetic anhydride the *ortho* compound is formed alone. This same *ortho* transformation is brought about, with some azoxy compounds at least, by the action of light.

The presence, the nature, and the position of substituents in the ring affect the nature of the transformation. Cusmano (61) found that o-aminoazoxybenzene with sulfuric acid gives phenylazimidobenzene

$$C_6H_4\Big\langle{\overset{N\diagdown}{\underset{N\diagup}{\mid}}}\Big\rangle NC_6H_5$$
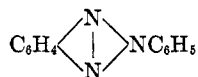
to the extent of 90 per cent yield, while at the same time a small quantity undergoes Wallach's transformation giving o-amino-p-hydroxyazobenzene.

Bamberger (62) found that sulfuric acid acting on his so-called iso-o-azoxybenzene, melting at 108–108.5°—one of the isomers—does not cause the Wallach transformation but acts as a reducing agent forming o-hydroxybenzeneazobenzene:
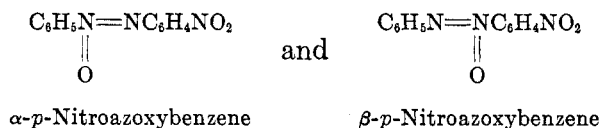
$$HOC_6H_4N{=\!=}NC_6H_5$$

Angeli (63) thought to find in Wallach's transformation a means of separating the two α and β isomers from one another. Of the two p-bromo compounds

$$C_6H_5N\!=\!NC_6H_4Br \qquad \text{and} \qquad C_6H_5N\!=\!NC_6H_4Br$$
$$\overset{\|}{O} \qquad\qquad\qquad\qquad\qquad \overset{\|}{O}$$
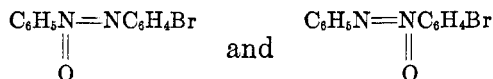
he expected the α form to undergo the transformation, the β form to be unattacked. In fact both of them give the same final product

$$HOC_6H_4N\!=\!NC_6H_4Br$$

when heated with sulfuric acid. This, according to Angeli, makes it very probable that the hot acid transforms the β into the α form which then undergoes transformation into the hydroxyazo compound. He found support for this view in the fact that nitric acid (density 1.45) acting on the two p-nitroazoxybenzenes

$$C_6H_5N\!=\!NC_6H_4NO_2 \qquad \text{and} \qquad C_6H_5N\!=\!NC_6H_4NO_2$$
$$\overset{\|}{O} \qquad\qquad\qquad\qquad\qquad\quad \overset{\|}{O}$$

α-p-Nitroazoxybenzene $\qquad\qquad$ β-p-Nitroazoxybenzene

nitrated only the β form, the $\overset{-N=}{\underset{O}{\|}}$ group protecting the benzene ring to which it is attached from the action of the acid. When, however stronger nitric acid (density 1.52) was used, both forms gave the same polynitro derivatives. To determine whether this action was due to the oxidizing nature of the acid he substituted chromic acid for nitric on the α and β forms of both p-bromo- and p-nitro-azoxybenzene. Both the α and β forms of the bromo compound and the α form of the nitro compound were unchanged by chromic acid but the β form of the latter was changed into the corresponding α form. He concluded, then, that when the β form was treated with sulfuric acid the following transposition took place:

$$\beta\ C_6H_5N\!\!=\!\!NC_6H_4Br$$
$$\overset{\|}{O}$$
$$\downarrow$$
$$\alpha\ C_6H_5N\!\!=\!\!NC_6H_4Br$$
$$\overset{\|}{O}$$
$$\downarrow$$
$$HOC_6H_4N\!\!=\!\!NC_6H_4Br$$
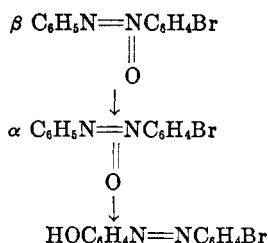
Possibly the β form took up an atom of oxygen and lost the one already present. That the chromic acid acted as an oxidizing agent was suggested by its reduction to a chromic condition. Further, that such an oxidation is possible was suggested by the discovery of Wohl (64) that azoxybenzene is capable of forming an unstable dibromo addition product, perhaps of the formula

$$C_6H_5N\!\!=\!\!=\!\!NC_6H_5$$
$$\overset{\|}{O}\ \ \underset{Br}{\diagup}\ \ \underset{Br}{\diagdown}$$
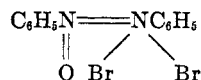
VI. BISAZOXY COMPOUNDS

Useful information concerning the possibility of isomerism of azoxy compounds may be found in the study of those bodies containing more than one azoxy groups. With this in view Angeli (65) treated bisazobenzene, previously prepared by Mills (65), with hydrogen peroxide and glacial acetic acid and obtained a yellow substance melting at 155°. It is apparent that there should be three possible isomeric forms of bisazoxybenzene (see figure 9).

The compound obtained by Angeli was very pure. To determine which of these three formulas should be ascribed to his compound he treated it with bromine and obtained a dibromo substitution product. Formula 1 should give no bromo derivative; formula 2 should give a monobromo derivative; and formula 3 shall give a disubstitution product. He therefore concluded that formula 3 should be ascribed to his compound. He further found that on reduction it gave the original bisazobenzene with which he started, showing that the reaction is reversible.

This bisazoxybenzene was treated with concentrated sulfuric

acid at 100° and was easily transformed into two products, both soluble in alkali with a red color. He assumed that they were the compounds represented in figure 10. One of these was so insoluble in all solvents as to make it impossible to characterize it, but the constitution of the other was established by synthesis. Aminoazobenzene was diazotized in the presence of hydrochloric acid and the product treated with phenol. The product was found identical with the new compound which must therefore have the formula 1 (figure 10). This formula he assigned to it.
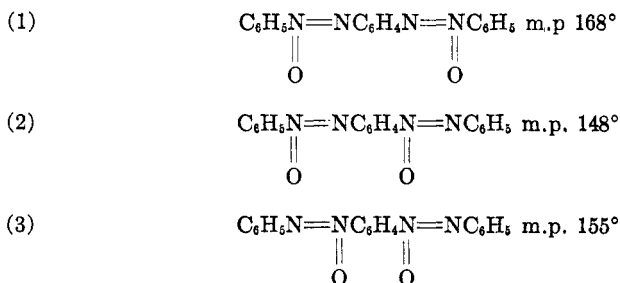
(1) $C_6H_5N=NC_6H_4N=NC_6H_5$ m.p 168°
$$\overset{\|}{O} \qquad \overset{\|}{O}$$

(2) $C_6H_5N=NC_6H_4N=NC_6H_5$ m.p. 148°
$$\overset{\|}{O} \qquad \overset{\|}{O}$$

(3) $C_6H_5N=NC_6H_4N=NC_6H_5$ m.p. 155°
$$\overset{\|}{O} \quad \overset{\|}{O}$$

FIG. 9. THE THREE POSSIBLE ISOMERIC FORMS OF BISAZOXYBENZENE

(1) $C_6H_5N=NC_6H_4N=NC_6H_4OH$

(2) $HOC_6H_4N=NC_6H_4N=NC_6H_4OH$
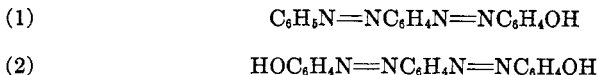
FIG. 10. SUBSTANCES FORMED BY THE ACTION OF CONCENTRATED SULFURIC ACID ON BISAZOXYBENZENE

The original bisazoxybenzene, melting at 155°, when treated with sulfuric acid at 0°, gave a very different product from that obtained at 100°. On prolonged treatment the compound disappeared and other products were formed—one insoluble in alkalies, orange-yellow in color; and a second, red in color, and soluble in alkalies with a reddish brown color, therefore a hydroxy derivative. The first product, that insoluble in alkalies, with proper solvents was separated into two compounds with melting points of 168° and 148° respectively. The yellow compound, with melting point 168°, when treated with sulfuric acid

at 100° gave the same monohydroxybisazobenzene given by Angeli's isomer (formula 3 in figure 9); on reduction with aluminium amalgam it gave the original bisazobenzene of Mills. It was unattacked by bromine and therefore Angeli concluded it was a bisazoxybenzene and was represented by formula 1 in figure 9.

The orange compound, melting at 148°, was obtained in small amount. It was unattacked by sulfuric acid at 0° and the author, noting the difficulties in its characterization, ascribed to it formula 2 (figure 9).

It is notable in this study of the bisazoxy isomers that peracetic acid, acting on bisazobenzene, gives only one of the three possible isomers—the one in which the oxygen atoms are attached to the nitrogens distant from the end nuclei. This is all the more notable since simple azo compounds under the action of peracetic acid give, in general, both isomers. The action of sulfuric acid is also unique in transforming one isomer into another. Though rare it has its analogy, as we have already seen, in the action of chromic acid on β-p-nitroazoxybenzene.

VII. TRISAZOXYBENZENES

The successful preparation of the bisazoxybenzenes was coincident with the preparation of trisazoxy compounds (65). Angeli found in azoxybisazobenzene

$$C_6H_5N=NC_6H_4N=NC_6H_4N=NC_6H_5$$
$$\overset{\|}{O}$$
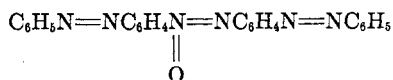
a starting point for their synthesis. This compound was prepared by Angeli by reducing p-nitroazobenzene with sodium alcoholate. It melted at 215°. Angeli apparently overlooked the fact that Borsch (67) had already made this compound by the action of alkali on quinonoximebenzoylphenylhydrazone and had found that it melted at 218°. Borsch had also prepared it by the action of sodium methoxide on p-nitroazobenzene, a method analogous to that used by Angeli. The agreement in melting point is not too satisfactory.

This compound was treated with peracetic acid and after boiling for several days there was obtained a golden yellow compound which melted at 230°. Four trisazoxybenzenes are possible (see figure 11).

Of these the one represented by formula 1 should be unaffected by bromine; those represented by formulas 2 and 3 should give monosubstitution products; while that represented by formula 4 should give a dibromo substitution product. The compound melting at 230° was treated with bromine in the cold with a trace of iron dust. It gave a dibromo substitution product and Angeli concluded, therefore, that its structure is represented by formula
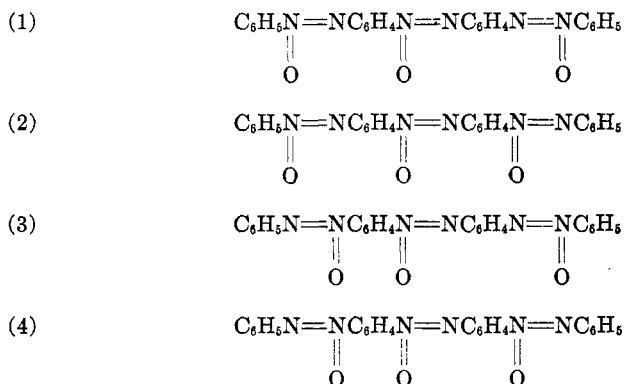
$$(1) \quad C_6H_5N=NC_6H_4N=NC_6H_4N=NC_6H_5$$
$$\qquad \qquad |\quad\quad\quad\quad || \quad\quad\quad\quad\quad ||$$
$$\qquad \qquad O \quad\quad\quad O \quad\quad\quad\quad O$$

$$(2) \quad C_6H_5N=NC_6H_4N=NC_6H_4N=NC_6H_5$$
$$\qquad \qquad\quad || \quad\quad\quad\quad || \quad\quad\quad ||$$
$$\qquad \qquad\quad O \quad\quad\quad O \quad\quad\quad O$$

$$(3) \quad C_6H_5N=NC_6H_4N=NC_6H_4N=NC_6H_5$$
$$\qquad \qquad\quad || \quad || \quad\quad\quad\quad\quad ||$$
$$\qquad \qquad\quad O \quad O \quad\quad\quad\quad\quad O$$

$$(4) \quad C_6H_5N=NC_6H_4N=NC_6H_4N=NC_6H_5$$
$$\qquad \qquad\quad || \quad || \quad\quad\quad ||$$
$$\qquad \qquad\quad O \quad O \quad\quad\quad O$$

Fig. 11. The Four Possible Isomeric Trisazoxybenzenes

4 (figure 11). Later Valori (68) prepared this compound by the oxidation of p-aminoazobenzene with peracetic acid.

Passerini (69) in an endeavor to make another of these trisazoxybenzenes started with the acetyl derivative of p-aminoazobenzene whose melting point, curiously, he reported as 157° though the literature gives it as 146°. This latter value Bigelow and McNevin (70) have corroborated by preparing the compound from pure aminoazobenzene and acetyl chloride. Passerini assumed that the acetyl group protected the amino group from oxidation and that on oxidation with peracetic acid he obtained the two corresponding acetylaminoazoxybenzenes. These he hydrolyzed with sodium hydroxide to obtain the corresponding

aminoazoxybenzenes. These were further oxidized with per-
acetic acid to give the trisazoxybenzene of Angeli, melting at
230°, and another melting at 223° to which he assigned the for-
mula 4 (figure 11). In figure 12 is illustrated in tabular form his

$$C_6H_5N=NC_6H_4NHCOCH_3$$

m.p. 157° (Passerini)
m.p. 146° (Literature)

H_2O_2

α $C_6H_5N=NC_6H_4NHCOCH_3$
$\overset{\|}{O}$

m.p. 166° (Passerini)
m.p. 151° (Bigiavi)

NaOH

α $C_6H_5N=NC_6H_4NH_2$
$\overset{\|}{O}$

m.p. 134.6° (Passerini)
m.p. 136° (Bigiavi)
m.p. 138.5° (Schmidt)

H_2O_2

$C_6H_5N=NC_6H_4N=NC_6H_4N=NC_6H_5$
$\overset{\|}{O}$ $\overset{\|}{O}$ $\overset{\|}{O}$

m.p. 223° (Passerini)
m.p. 242° (Bigelow and McNevin)

β $C_6H_5N=NC_6H_4NHCOCH_3$
$\overset{\|}{O}$

m.p. 142–3° (Passerini)
m.p. 172° (Bigiavi)

NaOH

β $C_6H_5N=NC_6H_4NH_2$
$\overset{\|}{O}$

m.p. 114° (Passerini)
m.p. 133° (Bigiavi)

H_2O_2

$C_6H_5N=NC_6H_4N=NC_6H_4N=NC_6H_5$
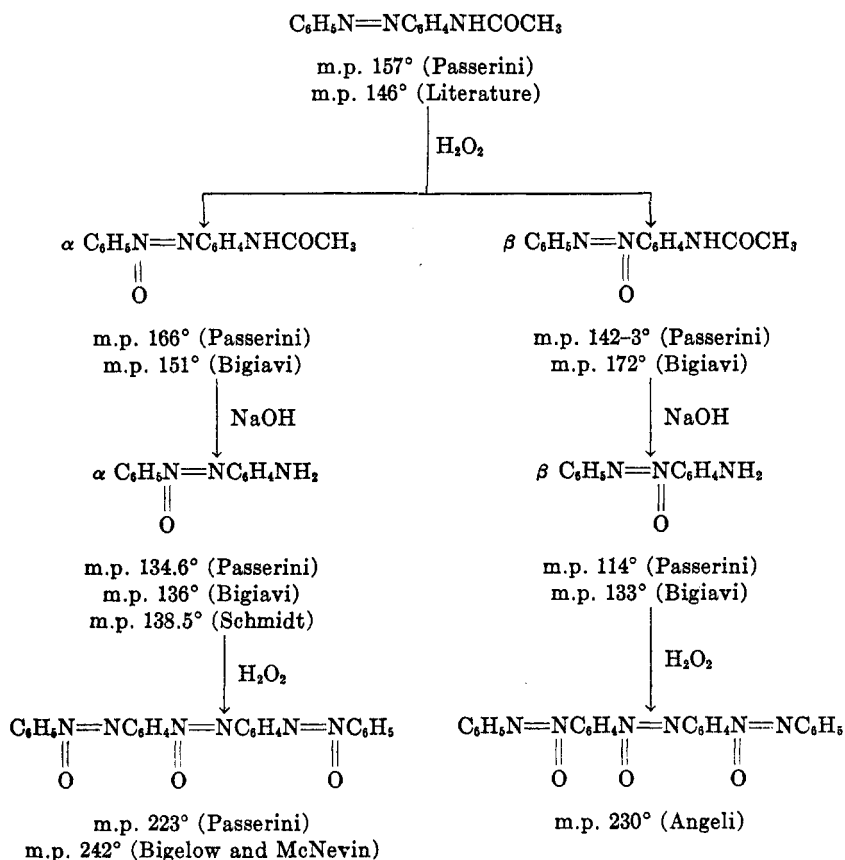$\overset{\|}{O}$ $\overset{\|}{O}$ $\overset{\|}{O}$

m.p. 230° (Angeli)

FIG. 12. SYNTHESIS OF TRISAZOXYBENZENES

process of synthesis with the melting points for the compounds
as found by him and others. Very evidently he was working
with impure products.

Bigiavi (71) has denied the accuracy of Passerini's primary
assumption that the acetyl group protects the amino group from

oxidation and has shown that, in fact, the amino group is partially oxidized to a nitro group, thus forming the two isomeric nitroazoxybenzenes as well as the isomeric p-acetylaminoazoxybenzenes. These facts would account for the differences in melting points of the various compounds formed and throw doubt on the accuracy of the melting point of the compound to which Passerini gave formula 1 (figure 11).

Further Bigelow and McNevin (70), by reducing p-nitroazoxybenzene with sodium arsenite, obtained as chief product of the reaction the new compound azobisazoxybenzene

$$C_6H_5N\!\!=\!\!NC_6H_4N\!\!=\!\!NC_6H_4N\!\!=\!\!NC_6H_5$$
$$\overset{\|}{O} \qquad\qquad\qquad \overset{\|}{O}$$
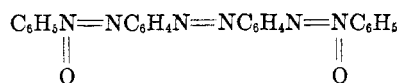
which was oxidized with peracetic acid and gave a golden yellow compound melting at 242°. Its analysis and properties showed it to be the trisazoxybenzene having the structure of formula 1 in figure 11 which Passerini ascribed to his compound with melting point 223°. By means of a new synthesis we are now seeking to further establish the structure of this compound.

Of the corresponding o-trisazoxybenzenes, Cusmano (72) has prepared one in small quantity by the action of a trace of sodium hydroxide on o-hydroxylaminoazoxybenzene. To it he ascribed the formula

$$C_6H_5N\!\!=\!\!NC_6H_4N\!\!=\!\!NC_6H_4N\!\!=\!\!NC_6H_5$$
$$\overset{\|}{O} \qquad\quad \overset{\|}{O} \qquad\quad \overset{\|}{O}$$
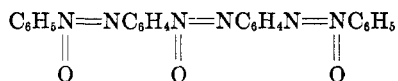
Charrier and Crippa (73) treated o-aminoazobenzene with peracetic acid for twenty-eight days and obtained three products, one of which, melting at 278°, they believed to be an o-trisazoxybenzene. It had the molecular proportions of such a compound and on reduction gave aniline and o-phenylenediamine, but they were not able to characterize it with certainty.
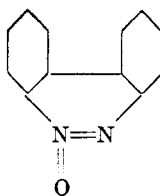
VIII. CYCLIC AZOXY COMPOUNDS

Only a few cyclic azoxy compounds have been prepared.

Täuber (74) succeeded in preparing a cyclic azoxy compound by reducing o-dinitrodiphenyl in an alkaline medium. Besides other

compounds he obtained one to which he ascribed the structural formula of an azoxy compound
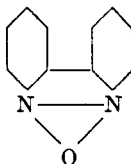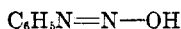

which today would be written

Ullman and Dieterle (75) in 1904 prepared the same compound and called it diphenazonoxyd. It might, perhaps, be better called cyclic *o,o′*-azoxydiphenyl. They prepared, also, the dimethyl derivative, the methyl groups being *meta* to nitrogen atoms.

Duval (76) and King (77) succeeded in preparing 4,4′-diamino-2,2′-azoxydiphenylmethane by reducing 2,2′-dinitro-4,4′-diaminodiphenylmethane with sodium sulfide in an alcoholic solution. Duval, also, in 1910 (78) prepared 2,2′-azoxydiphenylmethane-4,4′-dicarboxylic acid.

Arndt (79) prepared a substance which he considered a cyclic azoxy compound by boiling *o*-nitrophenylguanidine with dilute alkali. Ring closure was shown to occur through the elimination of water, the participating groups being the nitro and amino groups. The compound formed was 1,2,4-benztriazine-1-oxide which he considered an azoxy compound. Arndt and Rosenau (80) in 1917 were successful in preparing several cyclic azoxy compounds of this sort and found that they were capable of reduction to azo and hydrazo compounds and, further, that they could be regenerated from the azo compound by oxidation with hydrogen peroxide.

More recently Hussey, Marvel and Hager (81) have prepared ethyl-2,2'-azoxydiphenylmethane-4,4'-dicarboxylic acid by an interesting synthesis from benzophenone. This compound, having the structural formula

should be optically active and might, then, be capable of resolution into its isomers. The attempted resolution was not conclusive and the work is being continued.

IX. OXIDATION OF AZOXY COMPOUNDS

In general azoxy compounds are extremely resistant to oxidation. The special action of nitric, chromic and sulfuric acids has already been discussed. In these cases the action is not one of oxidation. With the hydroxyl-containing azoxy compounds, however, the situation is unique. They are oxidized with a considerable degree of ease with a breaking down of the ring.

Bamberger (82) found that both the *ortho* and isohydroxy-azoxybenzenes which have already been described were oxidized to isodiazotates by alkaline permanganate. So also was *p*-hydroxyazoxybenzene.

Angeli (83) studied the two *p*-hydroxyazoxybenzenes

| α Form | | β Form |

When the α form was heated with 2 per cent potassium permanganate in alkaline solution, oxidation began at once; Angeli noted

the odor of both nitrosobenzene and nitrobenzene and obtained the isodiazotate

$$C_6H_5N=N-OH$$

The β form was much more resistant to oxidation under the same conditions. Only on standing over night did he note reduction of the permanganate. He found in this fact a method for the separation of the β form in a condition free from the α form. Further, a study of the o-hydroxyazoxybenzenes of Bamberger proved that these show the same differences in ease of oxidation.

Angeli also treated p,p'-azoxyphenol with 2 per cent permanganate in alkaline solution until a permanent color remained. The filtrate from this mixture gave no color with β-naphthol. No diazo compound was formed, but oxalic acid was found in quantity.

Bigiavi and Poggi (84) oxidized benzeneazo-p-cresol
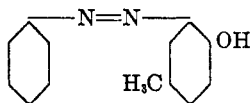
with peracetic acid and obtained the two isomeric α- and β-azoxy compounds
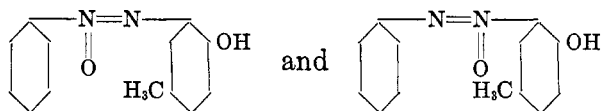
In alkaline permanganate solution these isomers showed the same general action as the corresponding α- and β-p-hydroxyazoxybenzenes. In this case the β form was oxidized to so slight a degree that the normal diazo compound obtained by acidifying the isodiazo compound gives but a feeble red color with β-naphthol.

This action of permanganate on the α and β hydroxyl containing azoxybenzenes is comparable with that observed in the action of bromine or nitric acid upon the isomeric monosubstituted compounds—an action already described—and illustrates again

the protective action of the oxygen of the azoxy group upon the nucleus to which it is adjacent.

X. NITRATION OF AZOXY COMPOUNDS

The usual method for preparing a substituted azoxy compound is to reduce, with a suitable reducing agent, the corresponding substituted benzene containing, in addition, a nitro group. Thus p-chloronitrobenzene on reduction with alcoholic potassium hydroxide (85) gives p,p'-dichloroazoxybenzene. The nitro group may be replaced by a nitroso or hydroxylamine group. Indeed there is a variety of methods, but the most general is to start with a nitro compound having the substituted groups desired and to transform it into an azoxy compound.

When more than one nitro group is present in the benzene compound reduced, then a nitrated azoxy compound is produced. Thus m-dinitrobenzene gives, on reduction with sodium methoxide, m,m'-dinitroazoxybenzene.
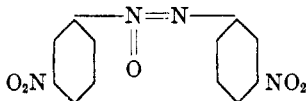
Similarly the *para* compound can be made (87) by the action of sodium hydroxide on p-dinitrobenzene.
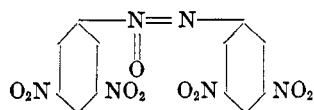
A further method for the preparation of nitrated azoxybenzene is that of direct nitration. It has already been pointed out that concentrated nitric acid will attack only one of the rings in azoxy compounds. The simplest compounds so formed are the mono-nitroazoxybenzenes discovered by Zinin (88). Both the *para* and *ortho* isomers are formed by treating azoxybenzene with concentrated nitric acid, keeping the mixture cooled. These isomers, of which the *para* is much the more abundant, are separated from one another with some difficulty.

The nitration of azoxybenzene with fuming nitric acid is attended with serious difficulties in separating the various products from one another, as various investigators have found.

From $2,4,4'$-trinitroazobenzene Werner and Stiasny (89) succeeded in making $2,4,4'$-trinitroazoxybenzene by treating the

azo compound with fuming nitric acid and chromic acid; by similar treatment of 2,4,3'-trinitroazobenzene, they prepared 2,4,3'-trinitroazoxybenzene. This method is unusual and is of special interest because of its analogy to the method of preparing azoxy compounds by oxidizing azo compounds with peracetic acid. These two trinitroazoxybenzenes were earlier made by Klinger and Zuurdeeg (90) in an interesting study of the nitration of azo and azoxy compounds.

The 3,5,3',5'-tetranitroazoxybenzene

$$O_2N \underset{NO_2}{\overset{N=N}{\bigcirc}} \underset{}{\overset{O}{\parallel}} O_2N \underset{NO_2}{\overset{}{\bigcirc}}$$

is made by reducing 1,3,5-trinitrobenzene with a concentrated sodium hydroxide solution (91).

The following section describes a further method of nitration of azoxy compounds applicable in the case of those containing a hydroxyl group.

XI. NITROUS ACID AND AZOXYPHENOLS

The protective action of the oxygen atom of the azoxy group toward the adjacent nucleus is shown also in the action of cold, dilute nitrous acid upon azoxyphenols. In this case again only the α isomer is attacked, the action being a particularly interesting one. Here the action is not one of oxidation but of nitration. For this action the presence of the hydroxyl group is a prerequisite.

Angeli, Bigiavi and Carrara (92) have shown that nitrous acid acts on the grouping

$$HOC_6H_4N=N-\underset{O}{\overset{\parallel}{}}$$
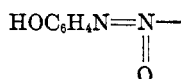
giving rise to a nitro derivative with the nitro group in the *ortho* position to the hydroxyl, while it is without action on the grouping

$$HOC_6H_4N=N-\underset{O}{\overset{\parallel}{}}$$
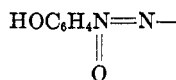
In harmony with these facts it has been found that azoxybenzene and β-p-azoxyphenol are not changed when excess of sodium nitrite is gradually added to their glacial acetic acid solution, while α-p-azoxyphenol and p,p'-dihydroxyazoxybenzene under the same conditions readily yield nitro derivatives.

Thus α-p-hydroxyazoxybenzene
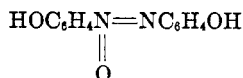
$$C_6H_5N=NC_6H_4OH$$
$$\overset{||}{O}$$
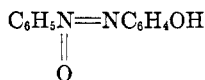
gives α-benzeneazoxy-p-hydroxy-m-nitrobenzene
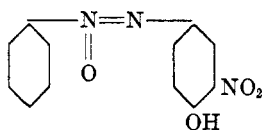
the corresponding β compound being unchanged.

The dihydroxy compound, p,p'-dihydroxyazoxybenzene
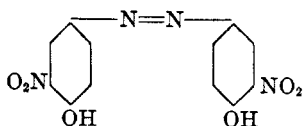
$$HOC_6H_4N=NC_6H_4OH$$
$$\overset{||}{O}$$

under the action of nitrous acid gives the mononitro derivative
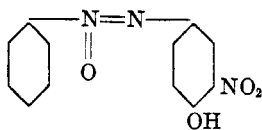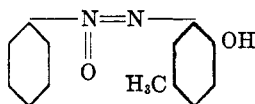

though p-dihydroxyazobenzene
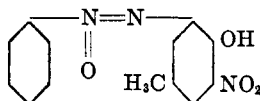
$$HOC_6H_4N=NC_6H_4OH$$

under the same conditions gives 3,3'-dinitro-4,4'-dihydroxyazobenzene

So also with benzeneazoxy-*p*-cresol

the corresponding benzeneazoxy-*o*-nitro-*p*-cresol

is obtained.

XII. THE ACTION OF LIGHT ON AZOXY COMPOUNDS

Wacker (93) found that when filter paper was impregnated with α-azoxynaphthalene dissolved in alcohol and placed in direct sunlight, it was colored red in a short time. The same was true also of the solution. He claimed, too, that azoxybenzene showed the same property though the action was slower. Knipscheer (60) stated that light acting on azoxybenzene gives *o*-hydroxyazoxybenzene. He obtained a yield of about 10 per cent by exposing sheets of filter paper impregnated with this compound to sunlight for five weeks. He believed that the action took place when the solid was exposed to light.

Baudisch and Fürst (94) noted the probable change, in sunlight, of α-azoxynaphthalene into α-hydroxyazonaphthalene. They then subjected the α-azoxynaphthalene in methyl alcohol to sunlight. After an hour brownish red needles were obtained which proved to be pure α-hydroxyazonaphthalene. Corresponding with this work of Baudisch and Fürst may be mentioned that of Cumming and Steel (16) which they believed gave evidence for the existence of two isomeric *o*-azoxynaphthalenes and of Cumming and Ferrier (18) who found that light on α-azoxynaphthalene gives the same hydroxyazonaphthalene found by Baudisch and Fürst above. Cumming and Ferrier studied the action of ultra-violet light on azoxybenzene and obtained a 30 per cent yield of *o*-hydroxyazobenzene.

Bigiavi and Sabatelli (95) found that the action of light on

α-benzeneazoxy-p-toluene, melting at 46°, gave a red substance, $m.p.$ 112–114°, which they regarded as probably the o-hydroxy compound.

The photochemical action of azoxy compounds has been little studied, though it is clear that it is a field offering many opportunities for research.   In particular it is desirable to determine with certainty whether or not the action of light causes isomerism. It would rather seem, at present, that the evidence does not strongly support belief in this hypothesis.

XIII. THE GRIGNARD REAGENT AND AZOXY COMPOUNDS

Concerning the action of the Grignard reagent on azoxy compounds very little seems to have been published.   Cumming and Ferrier (96) attempted to determine the best conditions for the interaction between ethylmagnesium iodide and azoxybenzene and found that the reaction products were azobenzene and a brown oil, which has the odor of ethylaniline but could not be identified as such.

XIV. PREPARATION OF AZOXY COMPOUNDS

Although a discussion of the preparation of azoxy compounds may not be pertinent to the title of this paper the subject is briefly introduced here because of its importance and more particularly because it throws light on the reduction of these compounds.

According to Haber's rule (97) the direct line of reduction of aromatic nitro compounds is represented as follows:

$$C_6H_5NO_2 \rightarrow C_6H_5NO \rightarrow C_6H_5NHOH \rightarrow C_6H_5NH_2$$
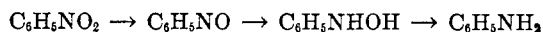
and azoxy compounds are formed by condensation of nitroso and hydroxylamine intermediates.   However true the primary assumption may be, there is much evidence to support the view that azoxy compounds are formed by the above condensation.

This condensation takes place best in alkaline solution.   Some have held the view (98) that, in acid solution, nitroso compounds are reduced with infinite velocity, precluding condensation. This view, however, is untenable since Flürscheim (99) has

shown that in numerous cases reduction may give rise to azoxy compounds even in the presence of strong mineral acids. Flürscheim and Simon (100) showed that both condensation and reduction of nitroso and hydroxylamine derivatives take place at measurable rates whether the solution be acid, neutral or alkaline. *A priori*, then, neither reduction of the intermediate compounds to amines nor condensation to azoxy compounds is excluded. It is possible, however, to vary the velocity of these reactions within wide limits so that one may be retarded to make another the primary or sole product.

Flürscheim and Simon considered that the primary determinant of the course of the reaction is the valence of the nitrogen in the hydroxylamine derivative formed. If trivalent, condensation is favored; if pentavalent, condensation will not take place and the amine will be formed. In an acid solution the nitrogen of the hydroxylamine will be pentavalent and so reduction to the amine will be the chief course of the reaction. Still other factors influence the course of the reaction, such as strength of the hydroxylamine base, the concentration of acid, the nature of the solvent, the relative concentration of nitro compound and reducing agent, the strength of reducing agent, the temperature, and the constitution of the nitro compound.

With respect to his last influence it is of interest to note the effect of negative substituents on the course of the reaction. Nitrobenzene gives no perceptible yield of azoxybenzene when reduced with stannous chloride even in the absence of acid; *p*-nitrobenzaldehyde, with its moderately negative aldehyde group, gives a small yield of *p*-azoxybenzaldehyde; but 3,5-dichloro-4-bromonitrobenzene, being still more negatively substituted, gives an almost quantitative yield of azoxy compound under similar conditions.

Though it is possible to reduce some nitro compounds to azoxy derivatives in acid solution, most of the methods for the preparation of the latter require an alkaline medium. These methods may be classified as those of condensation, oxidation and reduction and as such will be discussed.

Condensation

Merz and Coray (101) treated a mixture of aniline and nitrobenzene with solid potassium hydroxide. A vigorous reaction took place with the evolution of a combustible gas and the formation of a resinous mass from which azobenzene was obtained. The authors believed that azoxybenzene was also present. We have already discussed the work of Angeli in preparing azoxybenzene from these compounds through the agency of metallic sodium.

Fischer and Wacker (102) found that p-nitrosodimethylaniline condensed with phenylhydroxylamine in absolute alcohol to give p-azoxydimethylaniline. A similar reaction took place in potassium hydroxide solution. Using the hydrochloride of phenylhydroxylamine, however, the reaction product was dimethylphenylene diamine.

Bamberger and Renauld (4), as already stated, found that nitrosobenzene and phenylhydroxylamine condense to give azoxybenzene without by-products. In the same manner, using substituted phenylhydroxylamines and nitrosobenzene, they succeeded in preparing m-azoxytoluene, p-azoxytoluene, p-dichloroazoxybenzene, m-dibromoazoxybenzene and p-dibromoazoxybenzene, all symmetrical azoxy compounds. In each case azoxybenzene was formed as well. They concluded that the nitrosobenzene oxidized the hydroxylamine derivative to an azoxy compound and was itself reduced to azoxybenzene. It is interesting to note that by treating nitrosobenzene with benzylhydroxylamine they obtained bisazoxybenzyl, a compound with the proportions of an azoxy compound but with twice its molecular weight. They gave to it the structural formula

$$C_6H_5CH_2N\!\!-\!\!NCH_2C_6H_5$$
$$\mid \quad \mid$$
$$O \quad O$$
$$\mid \quad \mid$$
$$C_6H_5CH_2N\!\!-\!\!NCH_2C_6H_5$$
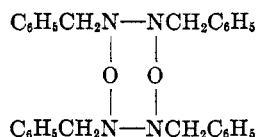
Later Bamberger and Bernays (103) by condensing phenylhydroxylamine and p-nitrosophenol to form p-monohydroxyazoxy-
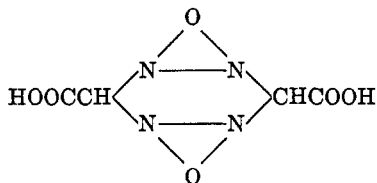
benzene and azoxybenzene showed, in fact, that mixed azoxy compounds could be made by a process of condensation. The reaction is, however, not a simple one, other products being formed as well.

Brand and Stohr (104) studied the effect of neutral, acid and alkaline media on the condensation of o-nitrosoacetanilide with o-hydroxyaminoacetanilide, dilute alcohol being the solvent. They found that the reaction was most complete in alkaline solution, less in acid and least in neutral.
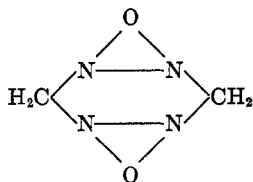
Oxidation

Petriew (105) prepared azoxybenzene by oxidation of azo benzene with chromic acid in an acetic acid solution in a closed tube at 150° to 250°. With nitric acid of specific gravity 1.54 azobenzene gave trinitroazoxybenzene, the azo group being oxidized and the rings nitrated as well.

Hantzsch and Lehmann (106) oxidized bisdiazoacetic acid to bisazoxyacetic acid, to which they gave the structure

$$\text{HOOCCH} \begin{array}{c} \\ \diagdown \end{array} \begin{array}{c} O \\ \diagup \diagdown \\ N{\longrightarrow}N \\ | \quad \quad | \\ N{\longrightarrow}N \\ \diagdown \diagup \\ O \end{array} \begin{array}{c} \\ \diagup \end{array} \text{CHCOOH}$$

From this they obtained on heating bisazoxymethane, with the structure

$$\text{H}_2\text{C} \begin{array}{c} \\ \diagdown \end{array} \begin{array}{c} O \\ \diagup \diagdown \\ N{\longrightarrow}N \\ | \quad \quad | \\ N{\longrightarrow}N \\ \diagdown \diagup \\ O \end{array} \begin{array}{c} \\ \diagup \end{array} \text{CH}_2$$

Bamberger and Tschirner (107) obtained azoxybenzene with other products by the oxidation of aniline with potassium permanganate in the presence of formaldehyde and sulfuric acid.

Bamberger and Hübner (108) oxidized *m*-nitroaniline with mono-persulfuric acid and obtained *m*-dinitroazoxybenzene and, in addition, *m*-nitronitrosobenzene and *m*-dinitrobenzene. From *p*-nitroaniline with the same reagent they obtained the corresponding azoxy derivative.

Werner and Stiasny (109) oxidized *p*-dinitroazobenzene to *p*-dinitroazoxybenzene by using fuming nitric acid at room temperature.

Prud'homme (110) oxidized aniline to azoxybenzene with hydrogen peroxide and obtained azoxybenzene. We have already described Angeli's method for the preparation of azoxy compounds by treating azo bodies with this reagent. Glacial acetic acid is the usual solvent used.

In alkaline solution Limprecht (111) oxidized *m*- and *p*-amino-benzenesulfonic acids with potassium permanganate and obtained the corresponding azoxybenzenemonosulfonic acids. With these, azo compounds were formed as well.

Bamberger (112) found that phenylhydroxylamine was oxidized to azoxybenzene when heated in the air on a steam bath. Wacker (113) found that *α*-naphthylhydroxylamine under the same conditions was oxidized to *α*-azoxynaphthalene.

Reduction

Flürscheim's assumption (99) that condensation of hydroxylamine derivatives and nitroso compounds to form azoxy compounds takes place best when the hydroxylamine derivative is in the free state, led him to the conclusion that the presence of substituting groups in the ring would favor this condensation even in the presence of acids. To determine the accuracy of this assumption he reduced a number of such substituted compounds in acid solution. *m*-Dinitrobenzene with stannous chloride and hydrochloric acid gas in absolute alcohol gave *m*-dinitroazoxybenzene in fair yield. Symmetrical trinitrobenzene, under similar conditions, gave a better yield of tetranitroazoxybenzene while *m*-dichloro-*p*-bromonitroazoxybenzene gave an almost quantitative yield of dibromotetrachloroazoxybenzene.

An alkaline medium is, however, the most effective in which to

prepare azoxy compounds. Many reducing agents are effective, among which sodium and potassium methoxides and ethoxides have been much used. Klinger and Pitschke (114) reduced *m*-dinitrobenzene to *m*-dinitroazoxybenzene with sodium methoxide. Lachmann (115) prepared azoxybenzene from nitrobenzene by this reagent and Heumann (116) used sodium ethoxide in reducing *p*-chloronitrobenzene to *p*-dichloroazoxybenzene.

deBruyn and Blanksma (117) treated *m*-dinitrobenzene with sodium acid sulfide in alcohol and obtained some *m*-dinitroazoxybenzene and *m*-nitroaniline. Blanksma (118) with sodium disulfide reduced *m*-dinitrobenzene to the corresponding azoxy derivative in almost quantitative yield. With the *para* compound an azo derivative was the principal product.

Meldola and Andrews (119) reduced *m*-nitroaniline with stannous chloride and sodium hydroxide and obtained *m*-diaminoazoxybenzene and other products.

With concentrated sodium hydroxide deBruyn (120) reduced *p*-dinitrobenzene to *p*-dinitroazoxybenzene and 1,3,5-trinitrobenzene to 3,5,3',5'-tetranitroazoxybenzene. With ferrous sulfate and sodium hydroxide Alway and Bonner (121) reduced *m*-nitrobenzaldehyde to *m*-azoxybenzaldehyde. Using 60 per cent sodium hydroxide and iron pyrites (122) the Bayer Co. found that, from nitrobenzene, a yield of 90 per cent azoxybenzene could be obtained. With zinc dust and sodium hydroxide Guitermann (123) reduced *o*-nitrotoluene in an alcoholic solution to azoxytoluene.

Using sodium amalgam in a small amount of alcohol Melms (124) found that nitrotoluene gave azoxytoluene. Evans and Fry (125) used magnesium amalgam as a reducing agent in alcohol. From nitrobenzene they obtained azoxybenzene in 90 per cent yield, and from *o*- and *p*-nitrotoluenes they obtained the corresponding azoxy compounds. Using methyl alcohol instead of ethyl alcohol nitrobenzene gave azobenzene, *m*-dinitrobenzene gave dinitroazoxybenzene and a small amount of the corresponding azo compound, while the *o*- and *p*-nitrotoluenes gave both the azo and azoxy compounds but principally the former.

Sodium arsenite has been used to a limited extent as a reducing

agent for nitro compounds. Loesner (126) prepared azoxybenzene from nitrobenzene with this reagent in a strong alkaline solution. Vorländer (127) in a study of liquid crystals, a phenomenon exhibited by a variety of azoxy compounds, prepared azoxybenzalacetophenone from nitrobenzalacetophenone with this reagent. Bigelow and Philp (128) found that sodium arsenite acting on m-nitrobenzaldehyde gave m-azoxybenzyl alcohol and m-azoxybenzoic acid. Evidently the Cannizaro reaction accompanied the reduction of the nitro group.

Electrochemical reduction of nitro compounds in acid solution gives, in general, amino compounds. If the acid used is sulfuric, or especially acetic, aminophenols are formed. Elbs (129) electrolyzed nitrobenzene in a strong sodium hydroxide solution between platinum and iron electrodes, using a current density of 8.33 amperes per square decimeter. He obtained a 60 per cent yield of hydrazobenzene. Using sulfuric acid instead of sodium hydroxide, benzidine was the principal product and with it a small amount of azoxybenzene. Hausmann (130) showed that the reduction of o-nitroanisol in alkaline solution gave azoxy and hydrazo compounds. Lob (131) using a platinum anode and a cathode of nickel in 2 to 4 per cent aqueous alkali and with a current density of 5 to 7 amperes per square decimeter obtained a yield of 90 per cent azoxybenzene from nitrobenzene. Elbs, however, (132) found that o- and p-nitrophenol, even in alkaline solution, gave the corresponding amines. Phenol ethers were reduced to azoxy compounds. Further, Häusermann and Schmidt (133) found that several nitrophenyl ethers gave analogous azoxy compounds as a result of electrolytic reduction. Lob (134) reduced a 5 per cent solution of o-nitrobenzoic acid in a 5 per cent sodium hydroxide solution at the platinum cathode of a divided cell with a current density of 4 amperes. The yield was 50 per cent azoxybenzoic acid with 5 to 10 per cent hydrazobenzoic acid. Brand and Stohr (135) reduced o-nitroacetanilide electrolytically in the presence of sodium acetate, ethyl acetate and water and obtained o-azoxyacetanilide. Elbs and Wogrinz (136) reduced m-nitroacetophenone in sodium acetate and alcohol, obtaining m-azoxyacetophenone and m-azoacetophenone.

When *m*-nitrobenzophenone was used an almost quantitative yield of azoxy compound was obtained. In no case was the ketone group reduced.

Brand and Steiner (137) studied the reduction of nitro compounds with hydrogen using palladium charcoal as the catalyst. Using 2 grams of nitrobenzene, 40 cc. of alcohol and 2 cc. of 2*N* sodium hydroxide they obtained only aniline; with 5 to 10 cc. of 2*N* sodium hydroxide, azoxybenzene and hydrazobenzene became the chief products. They obtained other azoxy compounds as well by this method. Using platinized calcium carbonate as the catalyst and hydrazine as the reducing agent, Busch and Schulz (138) reduced various nitro compounds in an alkaline solution. They found that the nature of the solvent exerted a notable influence on the course of the reaction. Increase in the quantity of the catalyst favored the formation of hydrazo and amino compounds. In methyl alcohol they obtained almost quantitative yields of azoxybenzene from nitrobenzene.

Though a neutral solution is, in general, less favorable than an alkaline or acid medium for the preparation of azoxy compounds, some cases are known in which they have been prepared in such a medium. Shoesmith and Taylor (139) using zinc and alcohol reduced *o*-nitrobenzyl alcohol to the hydroxylamine derivative and allowed this to oxidize in the air to *o*-azoxybenzyl alcohol. The *meta* and *para* compounds were prepared in the same way. The method is, of course, an indirect one. Bornstein (140) heated *p*-nitrosodimethylaniline with benzenesulfonyl chloride in benzene and obtained *p*-tetramethyldiaminoazoxybenzene. Nesbit (141) has shown that benzoin and some related compounds, in hot alcoholic solution under the influence of a trace of sodium ethoxide, reduce nitro compounds to azoxy compounds. The method is particularly satisfactory in the case of *para* compounds. With *ortho* or *meta* substituted compounds the yields are smaller. The difficulty with the process is the separation of the azoxy product from the diketone formed from the reducing agent. Azoxy compounds were formed from *p*-nitrobenzylideneaniline, *p*-nitrobenzonitrile, *p*-nitrocinnamic ester, *p*-nitrostilbene and others.

XV. REDUCTION OF AZOXY COMPOUNDS

We have shown, in the discussion on the preparation of azoxy compounds, that an alkaline medium is most favorable for good yields. In acid solution the tendency is to favor the formation of amines. One would expect, therefore, to find that azoxy compounds have been most commonly treated with acid reducing agents. This is, in fact, true. Most of the work done has been with the object of determining the constitution of the azoxy compounds studied, through the isolation of the amines formed in acid solution. We have already given some illustrations of this method. Numerous illustrations could be given but a few will suffice. With tin and hydrochloric acid azoxybenzene is reduced to aniline, p-dichloroazoxybenzene with stannous chloride is reduced to p-dichlorobenzidine and p-aminoazoxybenzene with tin and hydrochloric acid gives aniline and p-phenylene diamine. Trimethylazoxyaniline with tin and hydrochloric acid gives p-aminodimethylaniline and methyl-p-phenylene diamine. Bromoazoxytoluene with tin and hydrochloric acid gives p-toluidine and m-bromo-p-toluidine.

Other reducing agents have been used also. Gabriel (142) treated m-dibromoazoxybenzene with alcoholic ammonium sulfide and obtained m-dibromohydrazobenzene. Schmidt (143) from p-nitroazoxybenzene by means of the same reagent obtained p-aminoazoxybenzene and p-aminoazobenzene, the former in larger quantity. Brunnemann (144) reduced m-azoxydisulfonic acid with ammonium sulfide to the corresponding azo compound. Sodium amalgam gave the same product in aqueous solution, but sulfur dioxide in aqueous solution had no action.

Elbs (145) reduced azoxybenzene electrolytically in acid solution to p-aminophenol. In the same way Lob (146) reduced azoxybenzene in alcohol and concentrated sulfuric acid to benzidine. Mercury was used as a cathode. Elbs and Schwartz (147) by electrolysis reduced p-diamino-o-azoxytoluene in dilute alcoholic solution with sodium acetate to p-diamino-o-hydrazotoluene in good yield.

Meldola and Andrews (148) reduced m-diaminoazoxybenzene

in alcohol with zinc dust and sodium hydroxide to the corresponding hydrazo compound. On exposure to the air the hydrazo body was oxidized to the corresponding azo body, a very general reaction. With potassium hydroxide the reduction did not stop at the hydrazo stage. Instead, *m*-phenylene diamine was the chief product.

Bigiavi (149) studied the action of nitroxyl on azoxy compounds. He found that azo compounds were formed. Azoxybenzene gave azobenzene, *p*-dinitroazoxybenzene gave *p*-dinitroazobenzene and *p*-mononitroazoxybenzene gave *p*-mononitroazobenzene.

Flürscheim (150) reduced *m*-dinitroazoxybenzene in a boiling absolute alcohol solution with ammonium sulfide: *m*-Nitroaniline, *m*-dinitroazobenzene and *m*-dinitrohydrazobenzene were the products.

XVI. THE ISOMERISM OF THE DIAZOTATES

One of the most interesting phases of the theory held by Angeli concerning the structure of azoxy compounds is the view now held by him that this theory applies also to the diazotates, whose structure for many years has been believed best explained by the *syn* and *anti* isomerism suggested by Hantzsch. The views of Angeli, expressed in a number of published researches of recent years, have been vigorously combated by Hantzsch and most particularly in a recent paper (102). In view of the contentious nature of the subject we have thought it unwise to introduce it here.

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