developed. Results were compared with the molybdate method and agreed closely. There was no difficulty in determining the point of precipitation of the phosphate within 0.1 cc. when the ash was used. The ash was moistened with concentrated hydrochloric acid and the acid evaporated on the water-bath. It was then boiled with 50 cc. of distilled water and titrated with uranium solution. Under these conditions the end-point was always sharp. If the ash was not treated with hydrochloric acid, if acetic acid was substituted for hydrochloric acid or if, after treatment with hydrochloric acid, the ash was heated much above the temperature of boiling water, the phosphates were insoluble or, at least, remained in a form where they were not attacked by the uranium solution. With these precautions, the uranium method gives on a beer ash results which are quite accurate to 0.1 cc., and which are quickly obtained.

Sulphates.—The photometric method of Hinds[1] was used. In my hands his tables give percentages in beer ash more closely agreeing with the gravimetric than when the tables of Jackson[2] were used, as the latter yielded too high results. The solution of ash in hot, dilute hydrochloric acid, was either taken direct after filtering, or the filtered solution from the phosphoric acid determination could be equally well used.

Ash, Salicylic Acid, and Free Acid were determined by the usual official methods.

NEW HAMPSHIRE COLLEGE,
July 2, 1902.

ON AZOXYBENZENE.

BY ARTHUR LACHMAN.

A FEW years ago, I endeavored to deduce the structure of the nitro-group, and came to certain conclusions.[3] Subsequent developments, however, showed the line of reasoning then adopted to be erroneous; and these conclusions have since been withdrawn.[4] A new method of investigation became necessary, and a

[1] This Journal, **22**, 269.
[2] *Ibid.*, **23**, 799.
[3] *Am. Chem. J.*, **21**, 433 (1899).
[4] This Journal, **23**, 897 (1901).

study of azoxybenzene, one of the reduction-products of nitro-benzene, seemed to promise useful results. The present paper deals with the properties and the structure of azoxybenzene.

Azoxybenzene stands in a peculiarly intimate and important relation to nitrobenzene. First of all, in its general indifference to all but reducing agents, it closely resembles its mother-substance. Secondly, it still contains oxygen, and has no hydrogen directly attached to its nitrogen atoms. Thirdly, it is always the first, and usually the chief, product of alkaline reducing agents upon nitrobenzene. In view of this important relationship between these two substances, it is curious that so little is known about azoxybenzene. Its natural history is exceedingly meager.

Azoxybenzene was first prepared by Zinin,[1] by the action of alcoholic potash on nitrobenzene. Klinger, at a much later date, investigated the action of different alcohols and alkalies upon aromatic nitro-compounds,[2] and for the preparation of azoxyben-zene itself recommended the method still in common use,—reduc-tion of nitrobenzene with a solution of metallic sodium in methyl alcohol. Various other reducing agents have at times been pro-posed, such as alkaline stannites, sodium amalgam, etc.; but they do not give good yields with nitrobenzene, so far as I have tried them.

The chemical reactions of azoxybenzene have not been ex-haustively studied. Mild reducing agents, e. g., metallic iron,[3] remove oxygen, and leave azobenzene; more energetic agents re-duce azoxybenzene to aniline, whereby hydrazobenzene[4] often appears as an intermediate product. Aside from these more obvious reactions, only one has attracted more than a passing interest. When azoxybenzene[5] is warmed with concentrated sul-phuric acid, it is isomerized to p-hydroxyazobenzene:

$$C_6H_5—N_2O—C_6H_5 \longrightarrow C_6H_5—N=N—C_6H_4OH.$$
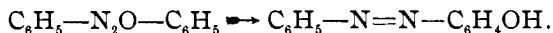
The mechanism of this reaction, which has not yet been satis-factorily explained, will be discussed below.

The data which I have gathered during my study of azoxyben-zene are here presented under the following heads:

[1] *J. prakt. Chem.*, **36**, 98 (1845).
[2] *Ber. d. chem. Ges.*, **15**, 865 (1882) ; **16**, 941 (1883).
[3] Schmidt and Schultz : *Ann. Chem.* (Liebig), **207**, 328 (1881).
[4] *Cf.* Meyer-Jacobson : "Lehrbuch," II, p. 251.
[5] Wallach : *Ber. d. chem. Ges.*, **13**, 525 (1880) ; **14**, 2617 (1881).

I.   The preparation of azoxybenzene.
II.   The action of sulphuric acid on azoxybenzene.
III. *p*-Hydroxyazobenzene-*p*-sulphonic acid.
IV.   Miscellaneous reactions of azoxybenzene.
V.   Some reactions of diphenylnitrosamine.
VI.   The constitution of azoxybenzene.

I. THE PREPARATION OF AZOXYBENZENE.

The reduction of nitrobenzene to azoxybenzene is best accomplished by the use of alcohols in alkaline solution.   As mentioned above, Zinin used ordinary alcohol and caustic potash.   This gives a rather impure azoxybenzene and an imperfect yield. Klinger obtained better results with sodium methylate dissolved in methyl alcohol.   The use of metallic sodium in large quantities, however, I found to be inconvenient as well as expensive, for the sodium must be added slowly to the alcohol.   A remark of Klinger's, that ordinary methyl alcohol often contains *much water*, suggested the direct use of sodium hydroxide; and it was soon found that a return to Zinin's method, simply changing alkalies and alcohols, gave much the best results.

It was also found, however, that to obtain good yields of azoxybenzene it is essential for the methyl alcohol to be absolutely ketone-free, whereas the amount of water present is relatively without influence.   In all the following experiments, the reagents (sodium hydroxide, methyl alcohol, nitrobenzene) were directly mixed, and gently boiled for three hours on a water-bath, a previous test having shown that a separate solution of the alkali before adding nitrobenzene had no influence upon the course of the reaction.

INFLUENCE OF WATER UPON YIELD OF AZOXYBENZENE.

Methyl alcohol acetone-free. cc.	Water. Per cent.	Sodium hydroxide. Grams.	Nitrobenzene. Grams.	Yield of azoxybenzene. Per cent.
800	4	160	120	83
200	8	40	30	75
200	13	40	30	83

In all three cases, the azoxybenzene was of a bright yellow color, and practically pure.

INFLUENCE OF ACETONE UPON YIELD OF AZOXYBENZENE.

Methyl alcohol. cc.	Acetone. Per cent.	Sodium hydroxide. Grams.	Nitrobenzene. Grams.	Yield of azoxybenzene. Per cent.
400	3	80	60	62
650	none	120	100	97
1000	none	200	150	95
650	2.7	120	100	62

In the first and fourth experiments, the azoxybenzene was dark brown, and contained aniline, unaltered nitrobenzene, and iso-nitrile.

Upon the basis of the above results, the preparation of azoxy-benzene is a simple matter. Boil a mixture of 1000 cc. acetone-free methyl alcohol, 200 grams sodium hydroxide and 150 grams nitrobenzene for three hours; distil off the alcohol, and pour the residue into cold water. Freeze the precipitated yellow oil in ice, and wash with water until free from alkali. Then melt the crystals in a little dilute hydrochloric acid to remove traces of aniline, freeze again, and wash free from acid. The resulting crystalline mass is crushed and dried in air, and is now sufficiently pure for nearly all purposes. Azoxybenzene may be recrystallized from alcohol or from ligroin.

SOLUBILITY OF AZOXYBENZENE IN LIGROIN (b. p., 70°-80°).

100 grams ligroin will dissolve at 0° 10.7 grams azoxybenzene.
100 grams ligroin will dissolve at 15° 43.5 grams azoxybenzene.

SOLUBILITY OF AZOXYBENZENE IN ALCOHOL (94 per cent.).

100 grams alcohol will dissolve at 0° 5.0 grams azoxybenzene.
100 grams alcohol will dissolve at 15° 11.4 grams azoxybenzene.

The solubility of azoxybenzene in hot ligroin is so great that when cooled to 0° the solution practically solidifies completely; for purposes of recrystallization it is best to make a saturated so-lution at the ordinary working temperature and then cool in ice.

II. THE ACTION OF SULPHURIC ACID UPON AZOXYBENZENE.

As mentioned above, Wallach found that hot, concentrated sul-phuric acid isomerizes azoxybenzene to p-hydroxyazobenzene. Another product of this reaction he found in azobenzene. Wal-lach's work was confined to the identification of these two sub-stances. In view of the great importance of properly under-standing intramolecular rearrangements, I devoted much time to

a study of the mechanism of this reaction, varying the experimental conditions within wide limits.

No intermediate compounds between azoxybenzene and hydroxyazobenzene could be discovered. When azoxybenzene and sulphuric acid are mixed, a dark red solution is formed, with slight evolution of heat. If the mixture is poured into water, azoxybenzene is recovered quantitatively. If allowed to stand in the cold for varying periods of time, the rearrangement proceeds slowly, and is not complete even after a week. If warmed on the water-bath, the reaction proceeds with greater or less velocity, depending upon so many factors that it seems hopeless to find any relationship between them. But in all cases, much the same products are formed in varying amounts, and with more or less unchanged azoxybenzene if the process be interrupted before completion.

Besides the products obtained by Wallach, I have isolated three others. An almost constant product is a black, amorphous powder, insoluble in all ordinary solvents, infusible, difficult to wash, and evidently a high molecular polymerization-product not far removed from free carbon. It contains nitrogen, however. Another product of the reaction is p-hydroxyazobenzene-p-sulphonic acid. A third product, usually in very small amounts, is an amylamine, probably normal. Its formation is to be explained by an opening of one of the benzene rings in azoxybenzene, with simultaneous oxidation of a carbon atom. Besides these substances, traces of one or more reducing compounds, probably aminophenol and related substances, are usually present; I have not been able to isolate them. Finally, the formation of o-hydroxyazobenzene described by Bamberger[1] not long ago could be verified.

These products are formed in amounts depending upon the following factors: the initial temperature of the reaction, the maximum temperature, the concentration of the acid employed, the ratio of sulphuric acid to azoxybenzene, the duration of the experiment, and finally, upon the size and the shape of the containing vessel. The last factor, which may seem captious, finds its explanation in a hitherto unnoticed circumstance; for the reaction of sulphuric acid upon azoxybenzene is strongly exothermic, and may proceed with explosive violence. Ten grams of

[1] *Ber. d. chem. Ges.,* **33,** 3192 (1900).

each substance were warmed on the water-bath; after eleven minutes, the mixture shot out of the flask, with evolution of much sulphur dioxide and oxides of nitrogen, and the formation of voluminous carbon fully twenty times the capacity of the flask. At least three times as much acid as azoxybenzene must be taken to avoid this violent result, as a number of tests showed. Even then, the temperature of the liquid rises above 200°. It is clear that under these circumstances the temperature of the mixture is largely dependent upon the amount of radiation to the outside, which again is a function of the size and shape of the vessel, as well as of the absolute amounts of material taken.

Just what the influence of temperature upon the final result may be, my experiments have not sufficed to determine. As already mentioned, the reaction proceeds slowly even in the cold. On the other hand, I twice carefully warmed a mixture of 10 grams each of sulphuric acid and azoxybenzene (the explosive mixture above) to 85° for ten and for twenty minutes, and recovered 97 and 92 per cent. respectively of unchanged azoxybenzene. The larger the ratio of acid to azoxybenzene, the lower the temperature at which the reaction completes itself; using 200 grams of acid to 10 grams of substance, complete action was obtained at a temperature not exceeding 74°.

It is unnecessary to detail each one of the numerous tests I have made of this reaction; the general conditions that seem to determine the amount of each product will suffice. First a brief account of the method of separation. After warming the mixture for the desired time, it is poured into cold water. Azobenzene, both hydroxyazobenzenes, and the black powder separate. The mixture is shaken out with ether, whereby the powder causes troublesome emulsions; after each extraction, it is best to filter the ether through the same funnel, where the powder finally collects. After being thoroughly washed with ether, the powder must be washed with water to remove sulphuric acid (which it holds tenaciously), and then dried in air. The ether extract is shaken out with dilute alkali to remove hydroxyazobenzene, and then distilled; azobenzene remains, with whatever unchanged azoxybenzene may be recovered. These two substances must be separated by crystallization from alcohol. The alkaline solution

of hydroxyazobenzene is precipitated with an excess of mineral acid, and the compound filtered, washed and dried in air. The original aqueous acid solution contains the sulphonic acid of hydroxyazobenzene, and amylamine. It is rendered alkaline with caustic soda and distilled with steam; the amine passes over very quickly, is collected in hydrochloric acid, and obtained as a salt by evaporation on the water-bath. The residual alkaline solution rapidly darkens in air, and shows reducing action towards ammoniacal silver nitrate, etc. To separate the sulphonic acid, it is rendered slightly acid with sulphuric acid, and boiled down sufficiently to give a saturated solution of sodium sulphate on cooling. The sodium salt of hydroxyazobenzene sulphonic acid separates, being rather insoluble in cold water and still less in sodium sulphate solution.

A. p-Hydroxyazobenzene.—The best yields of hydroxyazobenzene are obtained by using a somewhat diluted sulphuric acid, about 85 per cent. (corresponding to $H_2SO_4 + H_2O$), by taking from five to twenty times as much acid as azoxybenzene, and by keeping the temperature low. From 60 to 75 per cent. of the azoxybenzene may be obtained in its isomeric form. Freed from the ortho-compound as indicated below, and recrystallized from alcohol, it may be obtained in a state of great purity. For the *preparation* of hydroxyazobenzene, the synthetic method of Griess (from diazobenzene and phenol) is much simpler and quicker, as well as less expensive.

B. o-Hydroxyazobenzene.—This compound was first isolated by Bamberger,[1] It is volatile with steam, and can be readily separated from the para compound. From 40 grams mixed *o*- and *p*-hydroxyazobenzene (obtained from 75 grams azoxybenzene in various experiments), I separated 1.5 grams bright red *o*-hydroxyazobenzene (m. p. 81° before recrystallizing). Bamberger registered 190° at the moment of violent action, but as the fluid of the above yield.

C. The Black Powder.—The amount of this amorphous product varies within wide limits—from a trace to 30 per cent. of the azoxybenzene taken. It is formed in greatest amount when the temperature is high and the ratio of acid to azoxybenzene low.

[1] *Loc. cit.*

There is no reason to believe that this substance has a uniform composition. Nothing definite could be learned about it, except that it is in some way related to the formation of amylamine during the rearrangement. Five grams of the powder were heated with 40 cc. concentrated sulphuric acid to 100° for three hours; 0.09 gram amylamine hydrochloride was obtained. In another test, 3.2 grams of powder were heated in a sealed tube with diluted sulphuric acid (1:1): time, three hours; temperature, 220°; yield, 0.35 gram. In a third test, 3 grams were heated almost to fusion with strong caustic soda solution, and the volatile bases collected; 0.30 gram impure salt, giving slight aniline reaction, was obtained,

It seems likely that the powder contains the amylamine group pre-formed, and that the base is detached from the rest of the complex by the action of various agents,

D. Amylamine.—During the first experiments, the amount of amylamine hydrochloride obtained varied from 0.5 to 7 per cent. of the azoxybenzene taken, without affording any clue as to the determining factor. The above experiments with the black powder, and the observation of the high temperature accompanying the rearrangement, suggested the dependence of this product upon the high temperature. A direct trial gave ample confirmation of this view.

Twenty grams azoxybenzene and 45 grams concentrated acid were allowed to heat on the water-bath. An inserted thermometer registered 190° at the moment of violent action, but as the fluid then completely covered the stem, further reading was impossible. Much of the mixture was lost by the explosion, but the collected residues yielded 2.7 grams hydrochloride, a yield of 14 per cent. on the total amount of azoxybenzene.

Amylamine hydrochloride, as obtained by this curious method, forms white needles. It is very soluble in water and in alcohol, but is not deliquescent. With chlorplatinic acid it forms a very insoluble, yellow, prismatic powder, which cannot be recrystallized from water, for it is decomposed, with the separation of metallic platinum, considerably below 100°. Heated in the ordinary melting-point apparatus, it sublimes above 150°; heated quickly on platinum, it can be made to melt, but rapidly volatilizes

under these conditions.   It is the salt of a primary base, as shown
by the intense isonitrile reaction.   For analysis, the salt was re-
crystallized from water, and dried over sulphuric acid for a few
hours.

Analysis:

I.   0.2061 gram gave 20.1 cc. moist nitrogen at 20° and
      750 mm.

II.   0.2359 gram gave 0.2712 gram silver chloride.

	Calculated for $C_5H_{11}N\,H_2.HCl.$	Found.
Nitrogen	11.33	11.13
Chlorine	28.67	28.42
Atomic ratio N : Cl	1 : 1.006	

For lack of time, no experiments were made with the free base,
except to note that its boiling-point is about 100°, and that it is
quite soluble in water.   At some subsequent date, an attempt will
be made to study this base, and to work out this somewhat unusual
method of preparation.   Normal amylamine has been described
only by Hofmann,[1] and was evidently obtained by him in very
small amount.   As prepared above, the base seems to be quite free
from ammonia, as well as from secondary or tertiary bases.

E.   Hydroxyazobenzene Sulphonic Acid.—The formation of
this substance offers no difficulties of explanation; it is a simple
case of sulphonation.   This is usually a reaction with small
velocity; and in this instance, the amount of sulphonic acid pro-
duced depends more upon the time during which the substances
act upon each other than upon the ratio of acid to azoxybenzene.
The maximum yield observed in my experiments was 11 per cent.
of the sodium salt (of the weight of azoxybenzene taken).   This
yield can of course be greatly increased by prolonged heating.   A
more detailed study of this acid is given below.

F.   Azobenzene.—During   the   energetic   rearrangement   of
azoxybenzene, azobenzene is a constant product.   It is formed in
amounts varying from 30 to 60 per cent. of the original substance.
Being formed in such large quantity, it was by no means clear
that it is merely a by-product, as Wallach regarded it; and it was
hoped that a careful study of the formation of azobenzene would
greatly assist the explanation of how hydroxyazobenzene is formed.

[1] *Ber. d. chem Ges.*, **15**, 770 (1882).

For it is evident that we have three possibilities involved: azobenzene is formed from hydroxyazobenzene; hydroxyazobenzene is formed from azobenzene; or finally, that both are formed simultaneously.

The last possibility, that both are formed at the same time, is ruled out by one experiment. 8.3 grams azoxybenzene stood in the cold for six days, with 35 grams of sulphuric acid of the strength $H_2SO_4 + H_2O$. The products of this reaction were 5.2 grams hydroxyazobenzene and 3 grams unchanged azoxybenzene; mere traces of amylamine and of the sulphonic acid were also observed.

A choice between the first two possibilities was afforded by a direct experiment in which 5 grams of pure hydroxyazobenzene were heated on the water-bath with 20 cc. sulphuric acid $(H_2SO_4 + H_2O)$. The products were: Black powder, 0.05 gram; amylamine, unweighable trace of hydrochloride; unchanged hydroxyazobenzene, 3.85 grams; azobenzene, 0.70 gram; sulphonate, 0.45 gram.

It seems clear that the formation of azobenzene is the result of auto-reduction of hydroxyazobenzene; as oxygen is not given off, the black powder is to be regarded as the oxidation product. We have here a case similar to the auto-reduction and auto-oxidation of benzaldehyde under the influence of caustic potash,

$$2 \ C_6H_5CHO \ = \ C_6H_5CH_2OH + C_6H_5COOH,$$
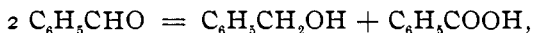
except that for hydroxyazobenzene the reaction is n-molecular rather than bi-molecular,

$$n \ C_6H_5N{=}NC_6H_4OH \ = \ (n{-}x)C_6H_5N{=}NC_6H_5 + \\ [x \ C_6H_5N{=}NC_6H_4OH.(n{-}x)O],$$
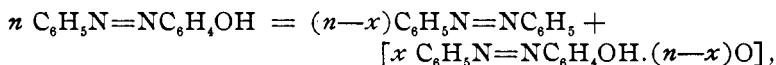
where n is a large number, and x a small one.

G. The Mechanism of the Rearrangement.—Further efforts to isolate intermediate products in the rearrangement of azoxybenzene proved futile. Adding acetic anhydride to the sulphuric acid gave results practically the same as above; the products were azo- and hydroxyazobenzene, and the black powder, the amine and the sulphonate being formed only in traces. The direct action of acetic anhydride was also tried; on heating azoxybenzene with it to 200° for five hours, a trace of hydroxyazobenzene was obtained,

but the bulk of azoxybenzene was recovered unchanged (4.8 grams from 5 grams).

A number of explanations have been offered for this rearrangement. Wallach and Belli[1] assume that the first products are phenol, diazobenzene sulphonic acid, and oxygen; and that the former then couple, eliminating sulphuric acid. The oxygen is not accounted for. Friswell and Green[2] similarly assume diazobenzene and phenol as the primary products, which then couple. Other, equally hypothetical explanations are quoted by Beilstein.[3] As I have found hydroxyazobenzene to be formed at temperatures much exceeding 100°, the assumption of a normal diazo reaction in hot sulphuric acid seems somewhat forced. If phenol were formed, its ready sulphonation would lead one to expect at least a small amount of some phenolsulphonic acid in the final product, but such is not the case.

I am inclined to regard the formation of hydroxyazobenzene in this reaction as a direct and immediate intramolecular rearrangement, as are so many other rearrangements of aromatic nitrogen compounds; there is no valid reason for assuming diazobenzene as intermediate. The other products of the reaction, as has been shown above, are secondary in their nature, and can all be obtained from pure hydroxyazobenzene.

It is interesting to note that Zinin, the discoverer of azoxybenzene,[4] tried the action of concentrated sulphuric acid upon this substance, but obtained only unchanged azoxybenzene together with some "gepaarte Schwefelsäureverbindung".

III. p-HYDROXYAZOBENZENE-p-SULPHONIC ACID.

The sulphonic acid obtained by the action of sulphuric acid upon azoxybenzene was subjected to closer examination, owing to certain discrepancies in the literature. By direct synthesis,[5] the action of diazobenzene-p-sulphonic acid upon phenol gives p-hydroxyazobenzene-p-sulphonic acid,

$$HO_3S—C_6H_4N=N—OH + C_6H_5OH =$$
$$HO_3S—C_6H_4N=NC_6H_4OH + H_2O.$$
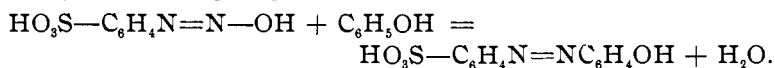
[1] Ber. d. chem. Ges., 13, 525 (1880).
[2] J. Chem. Soc. (London), 47, 923 (1885).
[3] Third Edition, Vol. IV, p. 1407.
[4] Loc. cit.
[5] Griess : Ber. d. chem. Ges., 11, 2192 (1878).

On the other hand, Wilsing[1] has described a sulphonic acid of the same constitution, but with different properties, which he obtained by the action of sulphuric acid upon azoxybenzene. In undertaking this work, Wilsing was guided by Wallach's recent discovery of the rearrangement to hydroxyazobenzene.

Wilsing's method of preparing his sulphonic acid was to heat azoxybenzene with fuming sulphuric acid (strength not given) to 110° for several hours, until a product completely soluble in water was obtained. In this way, he isolated not only a monosulphonic acid, but also a di-, tri-, and tetra-sulphonic acid. Wilsing himself carefully compared his own mono-sulphonic acid with the synthetic substance, and found many notable points of difference. The most striking difference was met in the action of bromine water; the synthetic product gave a precipitate of tribromphenol, whereas Wilsing's acid was indifferent even at 100°.

On the other hand, the sulphonic acid which I obtained above reacted readily with bromine water as indicated, and was found to be identical in every respect with the synthetic acid. Wilsing's acid cannot possibly have the constitution he assigned to it. In all probability he had azobenzene-sulphonic acid, for the conditions under which he worked (highly concentrated acid) are those which I have found to give chiefly azobenzene as the main product of the rearrangement. The discrepancies in Wilsing's analyses are easily accounted for by the fact that he analyzed the *anhydrous salts* of the acid. I have found the anhydrous salts of these sulphonic acids to be extremely hygroscopic; it is almost impossible to completely dehydrate them by ordinary methods, and the dehydrated salts will gain in weight even in a calcium chloride desiccator; an azobenzene sulphonate containing 1 molecule of water will, of course, give the same analytical results as an anhydrous hydroxyazobenzene sulphonate.

During this comparison I became interested in the manner in which tribromphenol is formed from hydroxyazobenzene sulphonic acid. I used the sodium salt, which was first prepared by Limpricht;[2] it contains 2 molecules of water:

0.7072 gram lost 0.0722 gram at 160°-170°.

[1] *Ann. Chem.* (Liebig), **215**, 228 (1882).
[2] *Ibid.*, **263**, 239 (1890).

	Calculated for $Na.C_{12}H_9N_2SO_4 + 2H_2O.$	Found.
Water	10.7	10.2

The salt requires 140 parts of water at 15° for solution, and crystallizes from hot water in golden yellow, glistening plates of very small size. The anhydrous salt is extremely hygroscopic; two samples, kept in separate calcium chloride desiccators over night, had each gained more than 5 mg.

The sodium sulphonate obtained from azoxybenzene had the same composition, and showed the same solubility.

0.5708 gram lost 0.0574 gram.

	Calculated.	Found.
Water	10.7	10.1

A. The Action of Bromine Water on Hydroxyazobenzene Sulphonic Acid.—When bromine water is added to a solution of this acid (or its sodium salt), a precipitate of tribromphenol is formed instantly. Exactly 6 atoms of bromine are taken up by 1 molecule of the salt. 1.06 grams synthetic sodium salt were titrated with standard bromine water (0.1918 N). When 99.1 cc. had been added, the solution was colorless, and did not smell of bromine; addition of 0.5 cc. bromine water caused a pronounced odor of bromine, which lasted after ten minutes' shaking. One molecule of salt required 6.02 atoms of bromine.

The tribromphenol was filtered and washed: Found, 1.01 grams; calculated, 1.04 grams. The filtrate on evaporation gave the sodium salt of phenolsulphonic acid. (Weighed after drying at 112°). Found, 0.65 gram; calculated, 0.62 gram.

An exactly similar result was obtained with the sulphonate obtained from azoxybenzene: 0.47 gram sodium salt gave 0.48 gram tribromphenol; calculated, 0.47 gram. The filtrate gave 0.29 gram sodium phenolsulphonate; calculated, 0.28 gram.

Finally, the free synthetic sulphonic acid was similarly treated, to make sure that the reaction was not confined to its salts. 0.50 gram sulphonic acid gave 0.56 gram tribromphenol; calculated, 0.59 gram.

The formation of phenolsulphonic acid during this reaction seemed mysterious at first; it was then found to be a secondary product, derived from an *intermediate diazo compound*. The solution, after the addition of bromine water, gives up exactly 1

molecule of diazo nitrogen when boiled (atmosphere of carbon dioxide).

Diazo nitrogen: 0.4579 gram synthetic sodium salt gave 30.7 cc. nitrogen at 13.5° and 741 mm.
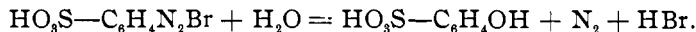
	Calculated.	Found.
Nitrogen	8.3	7.8

The diazo compound obtained here belongs to the normal, and not to the iso series. In two separate tests, the filtrate from the precipitated tribromphenol was run into alkaline β-naphthol, within less than twenty seconds from the first addition of bromine. In each case, immediate formation of an azo dye was noticed. The solution therefore contained normal diazonium-bromide-p-sulphonic acid.

The above analyses permit of a very accurate formulation of the action of bromine upon oxyazobenzene sulphonic acid. The first products are tribromphenol and the diazo compound:

$$HO_3S—C_6H_4N{=}NC_6H_4OH + 6Br = C_6H_2Br_3OH +$$
$$HO_3S—C_6H_4N_2Br + 2HBr.$$
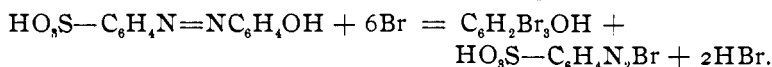
The second step consists in the hydrolysis of the diazonium salt:

$$HO_3S—C_6H_4N_2Br + H_2O = HO_3S—C_6H_4OH + N_2 + HBr.$$

These results are of interest from two points of view. In the first place, we have a reversal of the ordinary coupling reaction of diazo compounds. These react with phenols (in alkaline solution) to form azo dyes; here an azo dye (in acid solution) breaks down into a phenol and a diazo compound:

Diazo   Phenol
Alkali
Azo dye
Bromine
Phenol   Diazo
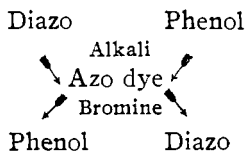
We have all the typical phenomena of a reversible reaction. This is all the more curious since we usually contrast the stability of azo compounds with the instability of diazo compounds; compare Meyer and Jacobson[1]: "Zünachst ist die grosse Beständigkeit (der Azoverbindungen) hervorzuheben, die im denkbar grössten Gegensatz zu der Unbeständigkeit der Diazoverbindungen steht".

[1] "Lehrbuch," Vol. II, p. 254.

An entirely similar result, for which the explanation is now at hand, was obtained by Witt,[1] who found that chrysoidine (diaminoazobenzene) gives phenol and nitrogen when heated to 150° with dilute hydrochloric acid.

In the second place, the above facts have some bearing upon the theories of Armstrong[2] and of Hewitt.[3] These investigators hold that hydroxyazo compounds possess two *isodynamic* (tautomeric) structures: in alkaline, or it may be neutral solution, or in any medium which fixes the hydroxyl group as such (*c. g.*, glacial acetic acid), we have true hydroxyazo compounds (as formulated above). In acid solution, however, the presence of derivatives of quinonephenylhydrazone is indicated; *c. g.*,

$$HO_3S—C_6H_4NH—N=C_6H_4=O.$$
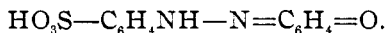
These authors have attacked the problem experimentally by studying the bromination of the oxygenated benzene ring; a para-substituted phenol is usually brominated in positions 2 and 6; quinone, on the other hand, would *add* bromine first in positions 2 and 3, then in 5 and 6. Thus Hewitt found that hydroxyazobenzene with bromine water gives di-*o*-bromhydroxyazobenzene, and concludes that it is a true hydroxy compound.

The same appears to be true to the hydroxyazobenzene sulphonic acid studied above, in spite of the much greater acidity of its solutions; for it also furnishes a di-*o*-substituted phenol. Another consideration leads to the same result. If we imagine tribromphenol formed from the tautomeric structure given above, the hydrazone molecule would form *iso*-diazobenzene-*p*-sulphonic acid,

$$HO_3S—C_6H_4NH—N=C_6H_4=O \rightarrow HO_3S—C_6H_4NH—NO,$$

whereas we really have a normal diazonium salt produced. We may conclude that there is no reason for assigning to hydroxyazobenzene-*p*-sulphonic acid any other structure than the one indicated by its name.

IV. MISCELLANEOUS REACTIONS OF AZOXYBENZENE.

A. The Action of Hydrochloric Acid upon Azoxybenzene.— Azoxybenzene is quite indifferent towards hydrochloric acid.

[1] *Ber. d. chem. Ges.*, **10**, 656 (1877).
[2] *Proc. Chem. Soc.*, **15**, 243 (1899); **16**, 158 (1900).
[2] *J. Chem. Soc.* (London), **77**, 810 (1900).

Upon heating 1 gram in a current of the dry gas to 100° for two hours, considerable gas seemed to be absorbed; but this escaped on brief exposure to the air, and the azoxybenzene was unchanged in weight and in melting-point.

Similar negative results were obtained upon heating azoxybenzene with concentrated hydrochloric acid solution (sp. gr. 1.20); four hours at 175° produced no change, nor did five hours at 200°. On heating another sample for eight hours to 225°, the azoxybenzene was completely changed, the tube contents were black, much tar was formed, some gas, and the solution gave reactions for phenol, aminophenol, and chlorinated aniline. No hydroxyazobenzene was obtainable. The reaction was not examined further. Werigo[1] has studied the action of hydrobromic acid upon azoxybenzene, and isolated only dibromaniline. From the action of hydriodic acid upon azoxybenzene he obtained some benzidine.

B. The Action of Hydroxylamine upon Azoxybenzene.—Four grams azoxybenzene were boiled with free hydroxylamine and a great excess of potash in methyl alcohol. After six hours, the mixture yielded 3.8 grams unchanged azoxybenzene, and traces of aniline and of azobenzene. Ten grams azoxybenzene were similarly heated in a pressure flask to 100° for sixteen hours. The mixture yielded 8.1 grams azobenzene (90 per cent. of theory), traces of aniline, 0.01 gram *o*-hydroxyazobenzene (m. p. 80°), and 0.02 gram *p*-hydroxyazobenzene (m. p. 150°).

From these experiments it is clear that the action of hydroxylamine upon azoxybenzene is very slow, and consists almost wholly of simple reduction. The formation of the isomeric hydroxyazobenzenes under these conditions is very interesting; but the amounts are very small.

C. The Action of Phenylhydrazine upon Azoxybenzene.—Ten grams azoxybenzene and 5 grams phenylhydrazine were heated to 110° for four hours. Aside from a slight evolution of ammonia, no action could be observed; and all of the azoxybenzene was recovered unaltered.

D. The Action of Zinc Ethyl upon Azoxybenzene.—Two grams azoxybenzene were allowed to stand with 4 grams of zinc ethyl for sixteen days; no action was observable, and all of the azoxyben-

1 *Ann. Chem.* (Liebig), **165**, 202 (1872).

zene (1.9 grams) was recovered. On heating azoxybenzene with zinc ethyl, a very complex reaction took place. 11.3 grams azoxybenzene were boiled with an excess of zinc ethyl (18 grams) in benzene solution. After one hour, 1000 cc. of gas had been evolved; in another hour, 100 cc. more were collected. This gas contained 27 per cent. ethylene; the balance consisted of ethane. On pouring into dilute sulphuric acid, a basic and a neutral oil were obtained. The basic oil (8 grams) contained aniline and ethyl aniline, and much tar; diethylaniline was carefully sought for, but not found. The neutral oil was directly distilled, and seemed to be thoroughly decomposed during this process. The liquid portion of the distillate seemed to be composed of about equal parts of aniline and ethylaniline. Here again diethylaniline was looked for,[1] but could not be detected. During the distillation, a combustible, basic gas was liberated, probably ethylamine.

No rational equation can be given for the action of zinc ethyl on azoxybenzene. A complex reduction occurs, and the nitrogen atoms seem to be separated. It is possible that in the neutral oil some intermediate product exists, but no suitable method for separating it could be found. This reaction will be the subject of renewed investigation later on.

V. SOME REACTIONS OF DIPHENYLNITROSAMINE.

For reasons to be given further on, it was necessary to subject diphenylnitrosamine to the same reagents used with azoxybenzene. In almost every instance, diphenylnitrosamine gave positive and decisive results under conditions where azoxybenzene gave negative or undecisive ones.

The action of zinc ethyl upon diphenylnitrosamine has already been carefully studied.[2] It will suffice here to summarize the results. When the two substances are brought together, an addition product is formed with almost explosive violence. This addition product, when treated with water, breaks down quantitatively into diphenylamine, diethylhydroxylamine, and zinc hydroxide.

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[1] The method of separation employed in this experiment consisted in the use of nitrous acid. The oil was treated with hydrochloric acid and sodium nitrite, after first adding ice and ether. The ethylaniline was immediately extracted as nitrosamine. The residual solution was halved; one part was precipitated with alkaline naphthol, and the azo dye weighed. The other part was distilled with dilute alkali, but gave no diethylamine (from possible nitrosodiethylaniline).

[1] Lachman : *Am. Chem. J.*, **21**, 433 (1899) ; *Ber. d. chem. Ges.*, **33**, 1022 (1900).

A. The Action of Hydrochloric Acid.—When dry hydrochloric acid gas is allowed to act upon diphenylnitrosamine, even at 0°, nitrosyl chloride is split off. The substance can be readily recognized by its characteristic properties, and when led into potassium iodide solution it liberates iodine and nitric oxide. A quantitative experiment showed that the whole of the nitroso group in diphenylnitrosamine is thus eliminated : 1 gram diphenylnitrosamine (dissolved in ligroin) was treated at 0° with hydrochloric acid gas, and the evolved gases conducted into potassium iodide. Air was carefully excluded by carbon dioxide, as otherwise much iodine is liberated by the catalytic action of nitric oxide. The iodine was titrated with sodium thiosulphate, after first driving out all nitric oxide.

	Calculated	Found.
Iodine ························	0.641	0.622

The action[1] is represented by the following equation :

$$(C_6H_5)_2N.NO + HCl = (C_6H_5)_2N.H + NOCl.$$
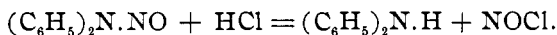
The diphenylamine left after the reaction is not pure, apparently owing to the formation of polymeric products.

B. The Action of Hydroxylamine on Diphenylnitrosamine.— Hydroxylamine and diphenylnitrosamine react in alkaline solution to form diphenylamine and nitrous oxide. Both of these products were obtained quantitatively. Four grams diphenylnitrosamine, 2 grams hydroxylamine hydrochloride, and an excess of methyl alcoholic potash were boiled until the evolution of gas ceased. The gas consisted of nitrous oxide (see below) and contained traces of nitric oxide, as shown by potassium iodide paper. The residual solution was evaporated and extracted with ether and then gave 3.4 grams pure diphenylamine (calculated 3.4 grams). No unchanged nitrosamine was left, for the diphenylamine solution. A direct test showed that less than 0.1 per cent. of nitrosamine in diphenylamine gave a deep blue color under these conditions. One gram nitrosamine was boiled with a slight excess of free hydroxylamine in an atmosphere of carbon dioxide (methyl alcohol solution). 113 cc. moist nitrous oxide were obtained (16° and 737 mm).

[1] See the explanation of this reaction which I have given : *Ber. d. chem. Ges.*, **33**, 1038 (1900).

	Calculated.	Found.
Nitrogen	0.22	0.20

In all probability, the first action of hydroxylamine on diphenyl-nitrosamine results in a normal, oxime-like condensation,

$$(C_6H_5)_2N.NO + H_2NOH = (C_6H_5)_2N.N{=}NOH + H_2O.$$
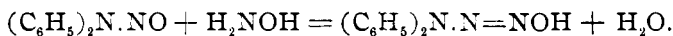
The intermediate product is unstable (it could not be isolated), and breaks down into nitrous oxide and diphenylamine,

$$(C_6H_5)_2N.N{=}NOH = (C_6H_5)_2NH + N_2O.$$
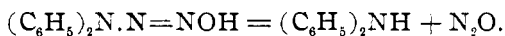
The reaction proceeds rapidly in the presence of free alkali, requiring not more than fifteen minutes; in the absence of alkali it takes about an hour.

C. The Action of Phenylhydrazine on Diphenylnitrosamine.—When molecular quantities of phenylhydrazine and diphenyl-nitrosamine are warmed on the water-bath, a violent reaction sets up. Much gas is liberated, and the mixture is shot out of the containing vessel. For the purpose of studying the reaction a little more carefully, two procedures were adopted. The first method consisted in carrying out the operation in sealed tubes. Four grams nitrosamine and 2.2 grams of phenylhydrazine were heated in an evacuated tube. After cooling, 420 cc. gas (corrected) were obtained. This gas was pure nitrogen; its weight is 0.53 gram (calculated for 1 molecule of nitrogen, 0.56 gram). The tube contents gave 3.2 grams diphenylamine, and a little aniline, the amount of the latter being too small to determine. No other products could be found in this or in several other similar experiments; benzene was carefully sought for, but no certain indication of its presence could be obtained.

The second method consisted in boiling the two substances in dry ether for from four to twelve hours. The gas given off under these circumstances contains considerable nitric oxide; if air has access to the flask, a little nitric acid[1] also forms. Nitric oxide also appears in small amount when the substances are heated in a sealed tube still containing air. Here again, no tangible product except diphenylamine could be isolated. From the same quantities as above 3.3 grams diphenylamine were found; calculated 3.4 grams.

[1] This was precipitated during the reaction as phenylhydrazine nitrate, which was analyzed. (Nitrogen found, 24.4 per cent.; calculated, 24.6.)

So far as the two products actually obtained are concerned, the equation may be written as follows:

$$C_6H_5NH—NH_2 + (C_6H_5)_2N.NO = (C_6H_5)_2NH + N_2 + ?(C_6H_5N).$$
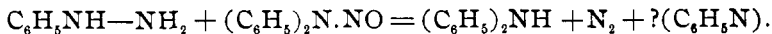
It seems, however, that as an actual fact less phenylhydrazine is used up than is called for by this equation; about one-fifth can be recovered as benzalphenylhydrazone after adding benzaldehyde. This interesting reaction will be studied more closely hereafter. In some respects it closely resembles the action of phenylhydrazine on aromatic C-nitroso compounds, recently investigated by Clauser[1]:

$$R—NO + C_6H_5NHNH_2 = R—N< + C_6H_6 + H_2O + N_2.$$
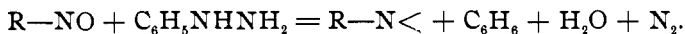
Reference should also be made here to the action of hydrazine (diamide)[2] on diphenylnitrosamine; reduction occurs, diphenylamine and asym.-diphenylhydrazine being the products.

VI. THE CONSTITUTION OF AZOXYBENZENE.

The structure usually assigned to azoxybenzene,

$$C_6H_5—\underset{\diagdown\diagup}{N—N}—C_6H_5, \qquad (I)$$
$$O$$
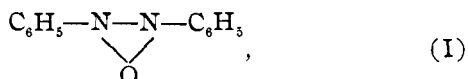
rests upon no direct evidence whatever, and within the last few years a number of authors[3] have suggested the following constitution as an alternative:

$$C_6H_5—N = N—C_6H_5 \atop \underset{O}{\|}. \qquad (II)$$
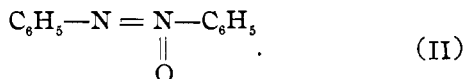
It must be said that as little direct evidence exists for this second structure as for the first. Brühl, to be sure, has found the refractive power of azoxybenzene to be greater than can be accounted for by (I), and even proposes a third structure as equally satisfactory to him:

$$C_6H_5—\underset{\diagdown\diagup}{N\equiv N}—C_6H_5. \qquad (III)$$
$$O$$
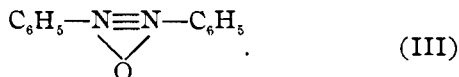
[1] *Ber. d. chem. Ges.*, **34**, 889 (1901). My own experiments were completed some months before Clauser's paper appeared.

[2] Cited in Beilstein, third edition, Vol. II, p. 339. I was unable to find the author and the journal reference.

[3] Meyer-Jacobson: "Lehrbuch," Vol. II. p. 251 (1894); Bamberger: *Ber. d. chem. Ges.* **29**, 2413 (1896); Brühl: *Ibid.*, **31**, 1361 (1898); **33**, 122 (1900).

I confess my inability to see any valid differences between (III) and (I) ; and the present discussion will be confined to formulas (I) and (II). Nor will Brühl's "spectro-chemical" data be considered at this time, for extrapolations of this sort weigh little as *evidence* when applied to wholly unknown atomic groupings.[1]

The general indifference of azoxybenzene to reagents renders it almost impossible to deduce its structure from its own reactions, and for the purposes of the present investigation, a comparative method was chosen. This consisted in the study of the behavior of diphenylnitrosamine towards the same reagents.

There is a very close resemblance between the structure of diphenylnitrosamine and formula (II) above, which is clearly shown by a slightly different method of writing:

$$C_6H_5\text{---}N\text{---}C_6H_5 \qquad\qquad C_6H_5\text{---}N \quad C_6H_5$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad |\diagup$$
$$N == O \qquad\qquad\qquad\qquad\qquad N == O$$

Diphenylnitrosamine.   Azoxybenzene (II).

In the first place, the two substances are isomeric; in the second place, each contains two phenyl groups; in the third place, each possesses two nitrogen atoms which are directly joined. Surely, if the similarity extends to the nitrogen-oxygen linking also, some slight similarity of behavior may be looked for in these two compounds.

Upon comparing the results reached above, however, we find that no similarity whatever exists. At $0°$, diphenylnitrosamine decomposes hydrochloric acid; at $200°$, azoxybenzene is unable to do so. At the boiling-point of methyl alcohol, the nitrosamine reacts promptly with hydroxylamine; azoxybenzene is indifferent to it, and is but slowly reduced to azobenzene at a much higher temperature. Diphenylnitrosamine reacts violently with phenylhydrazine; azoxybenzene does not react at all. Diphenylnitrosamine adds zinc ethyl with great energy in the cold: azoxybenzene, on the other hand, does not act at all in the cold, and undergoes complex decomposition when heated with this reagent. Showing no similarity in its reactions to diphenylnitrosamine, azoxybenzene cannot have a similar structure; and nothing remains but to regard the older formula (I) as

[1] See Hantzsch, *Ber. d. chem. Ges.*, **32**, 3148 (1899), for a similar opinion of the applicability of Brühl's data to nitrogen compounds.

the best expression of its chemical behavior; for, after all, the structural formula of a substance is but a condensed account of its chemical behavior.

Another line of reasoning also leads to the exclusion of formula (II). Azobenzene, $C_6H_5 — N = N — C_6H_5$, which contains the doubly linked nitrogen atoms assumed in that structure, reacts[1] with zinc ethyl with great violence, yielding ethylene and aniline, (the latter in almost theoretical amount). If azobenzene on the one hand, and diphenylnitrosamine on the other, react so quickly and smoothly with zinc ethyl, the indifference of azoxybenzene points to a marked diversity of structure.

A knowledge of the true structure of azoxybenzene is important from one general point of view: this substance represents the most stable known form of union between oxygen and nitrogen in organic compounds. The azoxy grouping we have just seen to be more inert than the nitroso group; it is more inert than the nitro group. The amine oxides are also much more active than azoxy compounds. If this inertness means anything at all, it indicates that in the grouping,

$$-\ddot{N}-\ddot{N}-$$
$$\diagdown\diagup$$
$$O$$
,
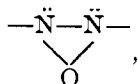
we have the most complete saturation of the affinities of oxygen and nitrogen for each other.

This is well shown by thermochemical data; azobenzene may be directly oxidized[2] to azobenzene, and the reaction is accompanied by the evolution of considerable heat[3]:

$$C_6H_5—N=N—C_6H_5 + O = C_6H_5—N—N—C_6H_5 + 257K.$$
$$\diagdown\diagup$$
$$O$$
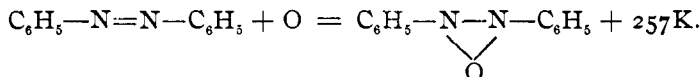
Contrast this with the negative heat of formation of the oxides of nitrogen; for example: nitrous oxide, $2N + O = N_2O — 180K$; nitric oxide, $N + O = NO — 216K$; $N + 2O = NO_2 — 77K$.

Having thus definitely established the constitution of azoxy-benzene, it will perhaps be justifiable to draw the general conclu-

[1] Frankland and Louis : *J. Chem. Soc.* (London), **37**, 560 (1880).

[2] Petriew : Beilstein. Vol. IV, p. 1348. See also the easy oxidation of dinitroazoben-zene to the azoxy compound ; Werner and Stiasny : *Ber. d. chem. Ges.*, **32**, 3263 (1899).

[3] Petit : *Ann. chim. phys.*, (6), **18**, 160 (1889).

sion that in its nitrogen compounds a bridged oxygen atom shows little tendency towards chemical action, and to apply this conclusion to the study of the valence-problem in other nitrogen-oxygen compounds.

SAN FRANCISCO, August, 1902.


DERIVATIVES OF PHENYLETHER.   III.

BY ALFRED N. COOK AND CHARLES F. EBERLY.

IN papers[1] previously published, accounts were given of the preparation of several derivatives of phenylether by the action of orthobromnitrobenzene upon ortho-, meta-, and paracresolates of potassium, and by reducing, oxidizing, and sulphonating the resulting compounds.   During the past few months the work has been continued and extended to the reaction between the cresols and parabromnitrobenzene with results as given in this paper and two others that will follow.

4-NITRO-2'-METHYL PHENYLETHER, $NO_2.C_6H_4$—O—$C_6H_4.CH_3$.

This compound was prepared by the action of parabromnitrobenzene upon potassium paracresolate (prepared by a method described in a previous article).[2]   The reaction is represented by the following equation :

$$NO_2.C_6H_4Br + KO.C_6H_4.CH_3 = NO_2.C_6H_4OC_6H_4.CH_3 + KBr.$$
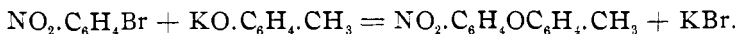
Molecular equivalents of the two reacting substances were heated in an oil-bath to $135°$ C.   An action began, as was shown by the agitation of the fused mass, which continued for some time as long as heat was applied.   When it was ended the temperature was raised to $160°$ without inducing any further action.   There remained a dark brown liquid and a copious precipitate of potassium bromide.   The yield was very good.

The nitro methyl phenylether was separated from the parabromnitrobenzene not acted upon, and other constituents, by fractional distillation under diminished pressure.   In a good vacuum it boils about $60°$ higher than parabromnitrobenzene and much higher than the other contaminating substances.

[1] *Am. Chem. J.*, **24**, 525-529 ; This Journal, **23**, 806-813.
[2] This Journal, **23**, 806.