[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Preparation of Methyl Substituted Azobenzenes and Azoxybenzenes and the Rearrangement of Methyl Substituted Azoxybenzenes

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In 1880 Wallach and Belli[2] found that heating azoxybenzene with concentrated sulfuric acid converted it to *p*-hydroxyazobenzene. Bamberger[3] has shown that about 0.25% of the ortho compound is formed also. Several other examples of this reaction have been reported. 4,4′-Dichloroazoxybenzene[4] gives only a trace of a phenol, but the 3,3′-isomer gives a high yield of a phenol which is probably 3,3′-dichloro-4-hydroxyazobenzene. Concentrated sulfuric acid produces a nearly quantitative yield of a phenolic product from 3,3′-dinitroazoxybenzene[5] but only a trace from 2,2′-dimethylazoxybenzene. Angeli[6] found that both isomers of *p*-bromoazoxybenzene rearranged to the same *p*-bromo-*p*′-hydroxyazobenzene. This work was confirmed by Bigiavi and Sabatelli,[7] who obtained *p*-methyl-*p*′-hydroxyazobenzene from both isomers of *p*-methylazoxybenzene. Finally, *p*-nitroazoxybenzene isomerizes to give a good yield of *p*-nitro-*p*′-hydroxyazobenzene.[8]

This investigation was undertaken to extend our knowledge of the Wallach rearrangement, particularly as regards the rearrangement of substituted azoxybenzenes. Methylazoxybenzenes of several types have been employed.

Symmetrically substituted azoxybenzenes were made by the reduction of nitrobenzenes and unsymmetrical ones by the oxidation of azobenzenes by peracetic acid.[9] Two methods were used in the preparation of the methyl azobenzenes. The first involved the coupling of an amine and a nitroso compound: $XC_6H_4NO + YC_6H_4NH_2 \longrightarrow XC_6H_4N{=}NC_6H_4Y$. The reaction gives satisfactory yields, except for ortho substituted compounds, but the necessary nitroso compounds are not always easily prepared.

The second method involved three reactions: a diazotized amine was coupled with an amine, the resulting azoamino compound was rearranged, and the amino group was removed. A serious limitation to the use of this reaction in synthetic work has been pointed out by Griess,[10] Goldschmidt,[11] and others. The hydrogen atom on the nitrogen chain of the azoamino compound may migrate from one nitrogen to another. Goldschmidt has proved the structure of many such compounds, so the reaction may be used in many cases.

In every case the structure of the aminoazo compound was proved by conversion to the sulfonamide followed by reduction to an amine (identified through the picryl derivative) and the monosulfonamide of a diamine (identified by mixed melting point with a sample made by standard methods).

It has been shown[7,8] that rearrangement of a para substituted azoxybenzene gives a hydroxyazobenzene with the phenolic group in the unoccupied para position. It has now been shown that if a methyl group appears in an ortho or meta position the hydroxyl group enters the para position of the same ring. In neither case could any isomeric product be isolated. The appearance of methyl groups in meta positions in both rings does not hinder the normal progress of the reaction. This is surprising in view of the observation that 2,2′-dimethylazoxybenzene gives only a trace of alkali-soluble material when subjected to conditions which normally cause rearrangement.[5]

The rearrangement of 4,4′-dimethylazoxybenzene was expected to be anomalous. Actually, two crystalline products were obtained. Analyses and molecular weight determinations indicate that both are possibly hydroxydimethylazobenzenes. Both form benzoates, so must contain hydroxyl groups. The solubility of one of them in alkali indicates the presence of a phenolic group. The other hydroxyl is evidently aliphatic in character for the compound is not alkali soluble.

The alkali-soluble compound might be 2- or 3-hydroxy-4,4′-dimethylazobenzene. McPherson[12] prepared the former through the reaction of 3-methyl-*o*-quinone with *p*-tolylhydrazine, and re-

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[1] Submitted as part of a thesis for the Degree of Doctor of Philosophy at the University of Illinois.

[2] Wallach and Belli, *Ber.*, **13**, 525–527 (1880).

[3] Bamberger, *ibid.*, **33**, 3192 (1900).

[4] Schultz, *ibid.*, **17**, 464 (1884).

[5] Klinger and Pitschke, *ibid.*, **18**, 2551 (1885).

[6] Angeli, *Gazz. chim. ital.*, **46**, ii, 82 (1916).

[7] Bigiavi and Sabatelli, *ibid.*, **57**, 557 (1927).

[8] Bigelow, *Chem. Rev.*, **9**, 139 (1931).

[9] Angeli, *Atti acad. Lincei*, [5] **19**, i, 793 (1910).

[10] Griess, *Ber.*, **7**, 1619 (1874).

[11] Goldschmidt, *ibid.*, **21**, 1019 (1888); *ibid.*, **21**, 2558 (1888).

[12] McPherson, THIS JOURNAL, **33**, 1529 (1911).

corded its melting point as 148°. He did not prove its structure. The phenol which would be formed through meta condensation in this reaction melts at 112–113°,[13] and our alkali-soluble product at 210–212°. The benzoates of the three melt at 93, 95, and 122–123°, respectively.

That the alkali-soluble compound is not 2-hydroxy-4,4′-dimethylazobenzene has been shown definitely by the synthesis of 2-ethoxy-4,4′-dimethylazobenzene, which is quite different from the ethyl ether of the compound in question.

A logical formula for the alkali-insoluble compound is that of 4-methyl-4′-hydroxymethylazobenzene. The appearance of the hydroxyl group in the side-chain, while not expected, is quite in keeping with other observations.[7,14]

Experimental

The symmetrical dimethylazoxybenzenes were prepared from the nitrotoluenes.[15]

Nitrosobenzene for the preparation of 2- and 3-methylazobenzenes was prepared by an improved method. Following the directions of Kamm,[16] 50 g. of nitrobenzene was reduced to phenylhydroxylamine. After filtering, the solution was cooled and an ice-cold solution of 42 cc. of concentrated sulfuric acid in 700 cc. of water was added slowly with vigorous stirring. Six hundred and forty cubic centimeters of cold 0.67 *N* solution of potassium dichromate was then added over five minutes. After fifteen minutes the precipitate was removed by filtration and distilled in steam, the condenser being chilled with ice. The yields of nitrosobenzene were from 55 to 60%.

2-Methylazobenzene.—A mixture of 21 g. of nitrosobenzene in 50 cc. of glacial acetic acid and 21 g. of *o*-toluidine in 50 cc. of absolute alcohol was kept at 40–50° for four hours. After standing overnight at room temperature a large volume of water was added and the oil which separated was extracted with low-boiling petroleum ether. After washing with hydrochloric acid and sodium hydroxide and removal of the ether, the oil distilled from 183 to 186° at 25 mm.[17] The yield was 20 g. (49%).

2-Methylazoxybenzene.—A mixture of 10 g. of 2-methylazobenzene in 50 cc. of glacial acetic acid and 2 cc. of perhydrol (30% hydrogen peroxide) was warmed for four to five hours to 60°, and was then allowed to stand at room temperature. Each day 1 cc. of perhydrol was added. After a week the solution was diluted with 250 cc. of water and extracted with petroleum ether. Evaporation of the petroleum ether left a light yellow oil which could not be crystallized or distilled in a vacuum. Analysis showed 13.15% nitrogen; calculated for $C_{13}H_{12}N_2O$, 13.22%.

In all cases in which the material could not be purified, a large excess of perhydrol was used to ensure complete oxidation.

3-Methylazobenzene and 3-methoxyazobenzene were prepared in the same way as the ortho isomers. 3-Methylazobenzene distilled at 185° at 24 mm. It gave orange crystals melting at 17–18°.[18] The azoxy compound was a light orange oil which could not be purified. Analysis indicated 13.12% nitrogen; calculated for $C_{13}H_{12}N_2O$, 13.22%.

4-Methyldiazoaminobenzene, 2,2′-dimethyldiazoaminobenzene, 3,3′-dimethyldiazoaminobenzene and 4,2′-[19] dimethyldiazoaminobenzene were prepared according to Mehner[20] and were rearranged to **4-methylaminoazobenzene, 2,3′-dimethylaminoazobenzene, 3,2′-dimethylaminoazobenzene and 4,3′-dimethylaminoazobenzene** by a modification of Goldschmidt's[11] process. A mixture of 30 g. of the diazoaminobenzene, 200 cc. of absolute alcohol, 30 g. of the appropriate amine and 3 g. of its hydrochloride was allowed to stand five days. It was then poured into two liters of 5% hydrochloric acid, and any unchanged diazoamino compound was destroyed by heating for an hour. The aminoazo hydrochloride which separated on cooling was filtered and converted to the free amine with ammonium hydroxide. The compounds were purified by repeated crystallization from 60% alcohol. With two exceptions, the melting points of these compounds checked those reported previously. 4,3′-Dimethylaminoazobenzene was found to melt at 131–132° [21] and the 3,2′-isomer at 85–86°.[22]

4-Methylazobenzene and 2,3′-Dimethylazobenzene.—The removal of the amino group of the aminoazo compounds offered some difficulty. The diazonium salts are quite stable, being only about half decomposed after standing for two days at room temperature.

A solution of 0.025 mole of the aminoazo compound in 50 cc. of hot alcohol was mixed with 6 cc. of concentrated sulfuric acid dissolved in 50 cc. of alcohol. The solution was cooled to room temperature and a solution of 1.8 g. of sodium nitrite in 5 cc. of water was added drop by drop below the surface of the liquid with vigorous stirring. A red precipitate of the diazonium salt separated. After half an hour 2 g. of copper bronze was added, whereupon nitrogen and acetaldehyde were evolved slowly. The mixture was slowly heated to boiling with vigorous stirring while 2 g. more of copper bronze was added in small portions. The solution was filtered and distilled with steam, the azobenzene distilling over a period of several hours. The *p*-methylazobenzene solidified in the distillate. The *o,m*′-dimethylazobenzene was a red oil which could not be distilled even in a vacuum without decomposition. The yields were about 50% by this method.

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(13) Nolting and Kohn, *Ber.*, **17**, 364 (1884).

(14) Klinger, *ibid.*, **16**, 943 (1883); Bender and Schultz, *ibid.*, **19**, 3237 (1886); O. Fischer and Hepp, *ibid.*, **26**, 2231 (1893); Schmidt, *ibid.*, **32**, 2920 (1899).

(15) The 2,2′-compound by the method of Guiterman, *ibid.*, **20**, 2016 (1887), the 3,3′-compound by an adaptation of Bigelow and Palmer, "Organic Syntheses," Vol. XI, 1931, p. 16, and the 4,4′-compound by a modification of the directions of Evans and Fry, THIS JOURNAL, **26**, 1164 (1904).

(16) "Organic Syntheses," Coll. Vol. I, 1932, p. 435.

(17) Löb [*Ber.*, **31**, 2205 (1898)] reported 185–186° at 28 mm.

(18) Jacobson and Nanninga [*ibid.*, **28**, 2548 (1895)] reported 175° at 19 mm. and 18–19°.

(19) In naming the diazoaminobenzenes the positions in the ring next to the —NH— group are indicated by (′). In naming the aminoazo compounds the positions in the ring containing the —NH_2 group are indicated in the same way. The nomenclature of the sulfonamides of the aminoazobenzenes follows the same system.

(20) Mehner, *J. prakt. Chem.*, **65**, 401 (1902).

(21) Mehner, ref. 20, reported 128°.

(22) Nietzki [*Ber.*, **10**, 1155 (1877)] gives 80°.

4-Methylazoxybenzene was prepared in the same way as 2-methylazoxybenzene and the two isomers[7] were separated by fractionation from glacial acetic acid.

Proof of Structure of the Aminoazobenzenes.—To 0.01 mole of the aminoazobenzene in 50 cc. of benzene were added 2 cc. of pyridine and 0.01 mole of benzene sulfonyl chloride. The solution was allowed to stand with occasional shaking for two days and was extracted with 5% sodium hydroxide. Upon acidification of the sodium hydroxide extracts the sulfonamide precipitated. It was purified by recrystallization from ethyl alcohol. Yields of 90% were obtained.

The sulfonamide of 4-methyl-4'-aminoazobenzene[23] showed 12.12% nitrogen (calcd. for $C_{19}H_{17}N_3SO_2$, 11.97%) and melted at 159°. The 2,3-dimethyl sulfonamide showed 11.75% nitrogen (calcd. for $C_{20}H_{19}N_3SO_2$, 11.51%) and melted at 138–139°. For the 3,2'-isomer these values are 11.62% and 144° and for the 4,3'-isomer, 11.78% and 152–153°.

Two grams of the sulfonamide, suspended in 100 cc. of water, was boiled for two hours with 10 g. of iron filings and 1 cc. of acetic acid. After filtering and cooling, the sulfonamide of the phenylenediamine precipitated and was recrystallized from water. The simple amine was steam distilled from the filtrate and was extracted from the distillate with benzene. The extract was heated to boiling and 1 g. of picryl chloride was added. After evaporation of the benzene, the picramide was recrystallized from ethyl alcohol. It was possible to detect and identify 0.2 g. of amine.

The sulfonamides and picramides were identified by mixed melting points with samples prepared by standard methods. In no case was any significant lowering of the melting point observed. The sulfonamides were prepared by reduction of the sulfonamides of the nitrobenzenes.[24] The 1-N-benzenesulfonyl-2-methyl-1,4-phenylenediamine melted at 145–146°, in agreement with the value 147° reported by Morgan and Micklethwaite.[24] 1-N-Benzenesulfonyl-3-methyl-1,4-phenylenediamine, which has not previously been reported melted at almost the same temperature —146°, but a mixture of equal amounts of the two showed a melting point depression of over thirty degrees. Analysis of the new compound for nitrogen showed 10.65%; calculated for $C_{13}H_{14}N_2SO_2$: 10.68%. The sulfonamide of 1-methyl-2-nitro-5-aminobenzene which was obtained as an intermediate melted at 139° and contained 9.65% nitrogen; calculated for $C_{13}H_{12}N_2SO_4$, 9.59%.

Rearrangement of Azoxybenzenes.—The rearrangement of the azoxybenzenes was performed as follows. A mixture of 5 g. of the compound and 50 cc. of 85% sulfuric acid was heated to 88° for ten minutes and was then poured onto 200 g. of ice. The hard, tarry product was heated with a liter of 5% sodium hydroxide for an hour. In every case there remained a residue which in most cases was tarry. The one exception was the case of 4,4'-dimethylazoxybenzene.

The sodium hydroxide solution was acidified and the light brown precipitate which formed was recrystallized from alcohol and from acetic acid. In some cases fractionally precipitating the material from glacial acetic acid with water concentrated the tarry material in the first or last fractions.

Identification of the Rearrangement Product.—The same method was used in all cases, except that of 4,4'-dimethylazoxybenzene.

The phenols were identified by comparing their melting points and the melting points of their ethyl ethers and benzoates with those recorded in the literature. In addition, the phenols were reduced to amines and aminophenols, and the amines were identified through their picryl derivatives. The aminophenols could not be definitely identified because of their instability.

4-Methylazoxybenzene.—The rearrangement of the two forms of the compound gave the same phenol, as Bigiavi and Sabatelli[7] have shown. Reduction of the phenol gave *p*-toluidine as the only simple amine.

3-Methylazoxybenzene was found to rearrange to 3-methyl-4-hydroxyazobenzene. The melting points of the phenol and its derivatives are: phenol, found 126–128°; recorded in the literature, 128–130°;[25] benzoate, found 109–110°; literature 110–111°;[13] ethyl ether, found 57–58°; literature 59°.[26] The picryl derivative of the amine obtained by reduction melted at 177°. Mixed with aniline picramide it melted at 178°. The yield of rearranged product was about 50%.

2-Methylazoxybenzene was converted to 2-methyl-4-hydroxyazobenzene; melting point of the phenol, found 109°; literature 109°;[13] ethyl ether, found 49°; literature 51.5°.[27] The picryl derivative of the amine obtained by reduction, alone or mixed with aniline picramide, melted at 178°.

3,3'-Dimethylazoxybenzene, upon rearrangement, gave 3,3'-dimethyl-4-hydroxyazobenzene. This melted at 116° and its ethyl ether at 47°. Jacobson[28] has reported 115° and 46–47° for these values. Reduction gave an amine whose picramide melted at 128°. Mixing with *m*-toluidine picramide did not change the melting point.

4,4'-Dimethylazoxybenzene gave a 20% yield of a product soluble in alkali and a 75% yield of an alkali-insoluble product. Both were readily purified to give crystalline products.

The alkali-soluble material, after crystallizations from benzene, acetic acid, and ligroin, melted at 210–212°. Analysis showed C, 74.38; H, 6.41; N, 12.41. Calcd. for $C_{14}H_{14}N_2O$: C, 74.30; H, 6.24; N, 12.39. Qualitative analysis showed the absence of sulfur. The molecular weight, as observed cryoscopically in camphor, was 207 (calcd., 226). Reduction gave *p*-toluidine as the simple amine.

On the supposition that the material was 4,4'-dimethylazobenzene with an hydroxyl group ortho or meta to the nitrogen bridge, attempts were made to synthesize the benzyl and ethyl ethers of these compounds. Unfortunately, only the ethyl ether of the ortho hydroxy compound was obtained. It melted at 76°. The ethyl ether of our alkali-soluble material melted at 50° and a mixture of the two at 34 to 43°. Analysis of the ethyl ether of the rearranged material for nitrogen: 11.37%; (calcd., 11.02%). The benzoate melted at 122–123°. It showed

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[23] For nomenclature, see footnote 19.

[24] Morgan and Micklethwait, *J. Chem. Soc.*, **87**, 80 (1905).

[25] Liebermann and v. Kostanecki, *Ber.*, **17**, 131, 877 (1886).

[26] Nolting and Werner, *ibid.*, **23**, 3259 (1890).

[27] Jacobson, *Ann.*, **287**, 147 (1895).

[28] Jacobson, *ibid.*, **287**, 184 (1895).

8.50% nitrogen (calcd., 8.31%). The benzyl ether melted at 123° and showed 8.94% nitrogen (calcd., 8.86%).

Preparation of 4,4′-Dimethyl-2-ethoxyazobenzene.—1-Methyl-3-hydroxy-4 nitrobenzene[29] was converted to the ethyl ether through the silver salt.[30] This was reduced by boiling with iron filings and dilute acetic acid. The amino ether after extraction with petroleum ether was coupled with *p*-nitrosotoluene[31] as outlined above. The product was extracted with petroleum ether and was crystallized from alcohol. Analysis showed it to contain 11.14% nitrogen; calcd., 11.02%; melting point, 76°.

Attempts to prepare the benzyl ethers of the ortho and meta hydroxy compounds and the ethyl ether of the meta compound by similar condensations led to tars.

Examination of the Alkali-insoluble Rearrangement Compound.—This material was crystallized from benzene, acetic acid and 75% alcohol as orange scales which melted at 208–210° with apparent decomposition. Analysis showed C, 74.66; H, 6.38; N, 12.28; calcd. for $C_{14}H_{14}N_2O$: C, 74.30; H, 6.24; N, 12.39. The molecular weight, observed cryoscopically in camphor, was 190 (calcd. 226). The observed value is too low, but the accuracy of the method is only 10%. At least the compound is not a polymer of a substituted azobenzene.

The benzoate of the alkali-insoluble compound melted at 121–122° and showed a nitrogen content of 8.36%; (calculated for the benzoate of a dimethyl azobenzene containing one hydroxyl group, 8.48%).

The alkali-insoluble compound was reduced by iron filings and acetic acid. The only reduction product which could be identified was *p*-toluidine, which was present in large amount.

Summary

1. A new method of synthesizing some unsymmetrical methylazobenzenes has been developed.

2. The well-known method of preparation of nitrosobenzene from nitrobenzene through the intermediate phenylhydroxylamine has been simplified and improved.

3. Some methyl substituted azoxybenzenes have been subjected to the Wallach rearrangement and the following observations have been made. (a) If the para positions are not filled by substituents the hydroxyl group will appear in the para position. (b) In the cases of mono-ortho and mono-meta methylazoxybenzenes the hydroxyl group enters the para position of the substituted ring. (c) If both para positions are filled, two products are obtained. One of them is soluble in alkali and the other is not. They may be 3-hydroxy-4,4′-dimethylazobenzene and 4-methyl-4′-hydroxymethyl-azobenzene.

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[29] Schultz, *Ber.*, **40**, 4322 (1907).

[30] Staedel and Kolb, *Ann.*, **259**, 224 (1890).

[31] Bamberger and Brady, *Ber.*, **33**, 274 (1900).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride.[1] XII. The Preparation of Esters of Aromatic Acids

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In an earlier paper[2] the preparation of esters of aliphatic acids was described. The purpose of the present investigation is to extend the study of this process to the formation of esters of aromatic acids and to consider the effect of various factors upon the yield of the esters.

The yield of ester increases as the quantity of boron fluoride used is increased until a maximum yield of ester is reached. The quantity of boron fluoride beyond this point is ineffective and in certain cases is deleterious to the quantity of ester formed. The amount of boron fluoride necessary to give a maximum yield is dependent upon the nature of the substituent in the benzene nucleus. For example, with benzoic acid a maximum yield of 85% is obtained when 14 g. of boron fluoride is used, while a maximum is reached only after 70 g. of the same agent is used for certain substituted benzoic acids, compared on a one-half mole acid basis. With *p*-aminobenzoic acid it is necessary first to add equimolar quantities of boron fluoride before any ester is formed, the maximum of 53% being reached when three moles of boron fluoride is used for each mole of acid. The reluctance of the first mole of boron fluoride to act as an esterifying agent is undoubtedly due to the formation of a stable coördinate covalent compound between the agent and the nitrogen of the amino group in the *p*-aminobenzoic acid. It is also worthy of note that methyl anthranilate can be produced in a yield of 85% by employing two moles of boron fluoride for each mole of acid. Here again the first mole of boron fluoride is ineffective toward ester formation.

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[1] For previous paper see, Croxall, Sowa and Nieuwland, THIS JOURNAL, **57**, 1549 (1935).

[2] Hinton and Nieuwland, *ibid.*, **54**, 2017 (1932).