(*b*) 1-Paratolyl-2-isoamoxymethylthiourea (m. 119°) was obtained when 1-paratolyl-2-ethoxymethylthiourea was crystallized from isoamyl alcohol (Kjeldahl):

Calculated for $C_{14}H_{22}ON_2S$: N, 10.52; found, 10.56.

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# PHENYL ETHER AND SOME OF ITS DERIVATIVES.

By Alfred N. Cook.

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## Bromination of Phenyl and Tolyl Ethers.

The ethers employed were all prepared by distilling the aluminium salts of the corresponding phenols. While the yield of phenyl and metatolyl ether was good, the yield of the ortho- and paratolyl ether was so small that, in some instances, it was found difficult to obtain a sufficient amount of some of the bromine derivatives to purify sufficiently to yield very satisfactory results on analysis, which accounts for some instances given below where there is considerable difference between the results of analysis and the requirements of calculation. The best yield of phenyl ether was obtained by distilling aluminium phenolate with a sharp heat; but in case of the tolyl ethers, the best yield was obtained by distilling with a low heat. A sharp heat gives rise to a greater proportion of higher boiling substances and less of the ether.

On distilling some aluminium paracresolate with a sharp heat, a peculiar phenomenon was observed, which was not noted in connection with the distillation of any other aluminium salt of the phenols. Bright flashes of light followed one another in quick succession on the surface of the boiling and decomposing liquid. This recalls the fact noted in connection with the distillation of aluminium phenolate in the preparation of phenyl ether, that the escaping gases occasionally ignited spontaneously on coming in contact with the air. In the present case, however, the evolving gases had not yet come in contact with oxygen and the phenomenon could not have been due to combustion.

On distilling some aluminium paracresolate which had been kept for a couple of months in a bottle with a defective cork, through which air had gained access and acted upon the substance, it was found that it yielded paracresol and almost no paratolyl ether and higher boiling substances. It did not melt down as the freshly prepared substance does, even when highly heated. It was found to dissolve very readily in absolute alcohol, carbon disulphide and various other organic solvents. On adding a little water to the solution there was thrown down a voluminous gelatinous precipitate. Its action is therefore exactly analogous to that of aluminium phenolate to which air in limited amount has had access for some time, and which has been described in a previous paper. *An* *investigation into the character and causes of these changes is now in progress in the chemical laboratory of the University of South Dakota.*

*Bromination of Phenyl Ether.*—Hoffmeister[1] prepared dibromophenyl ether by slowly adding bromine to phenyl ether dissolved in carbon disulphide, kept well cooled until the red color of the bromine ceased to vanish. Melting point, 55°. In an endeavor to prepare a higher bromine derivative, I added a large excess of bromine to some phenyl ether and allowed it to stand for three days with occasional shaking. The carbon disulphide was removed by evaporating on the water bath, which operation also removed a portion of the bromine not acted upon. The remainder of the excess of bromine was removed by washing with caustic soda solution. There was obtained a light yellow liquid of the consistency of glycerol, which failed to solidify on standing three months. It boiled at 240-260° at 30 mm. On analysis it yielded 59.6 per cent. of bromine. Theory would require 65.84 per cent. for the tetrabromo derivative and 48.78 per cent. for the dibromo derivative. It was apparently a mixture of the dibromo and tetrabromo derivatives, 36.5 per cent. of the former and 63.5 per cent. of the latter. From the experiments described below, one would not expect that a higher bromide would be found in the mixture.

*Tetrabromophenyl ether* ($(C_6H_3Br_2)_2O$) was prepared by gradually adding an excess of bromine to phenyl ether dissolved in carbon disulphide, to which had been added a little iodine to act as a carrier, and shaking meanwhile. The addition of iodine greatly facilitated the reaction, which was clear cut and rapid. In the beginning hydrobromic acid was given off very rapidly but gradually subsided and seemed to cease when sufficient bromine had been added to form the tetra compound. The solution was allowed to stand at room temperature for some time and then heated on the water bath to drive off the carbon disulphide and excess of bromine. There was obtained a red, viscous substance which became milk-white on washing with a solution of caustic soda, and on stirring with cold water it suddenly solidified. The yield of the crude product was quantitative and quite pure It distilled at 280–290° at 25 mm. and at 410–425° under ordinary atmospheric pressure. It is soluble in carbon disulphide and petroleum ether and insoluble in water, alcohol and most organic solvents. It crystallized in large, radial aggregations of swordlike needles The crystals obtained were about three-fourth inch in diameter. On cooling, *per se*, it likewise collects in radial masses on solidification. It is odorless and tasteless and colorless, but on continued exposure to light it turns slightly brownish. It melts at 83–84°. On analysis it yielded 65.56 per cent. of bromine. Calculated for $(C_6H_3Br_2)_2O$, 65.85 per cent.

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[1] *Ann.*, 159, 210.

Attempts were made to prepare the hexabromo, octobromo and decabromo derivatives. A little more than the calculated amount of bromine in each case was allowed to stand in contact with phenyl ether in the presence of iodine for several days with occasional shaking. In every case there was obtained only the tetrabromophenyl ether as shown by the melting point and analysis for bromine.

*Dibromometatolyl ether* ($CH_3C_6H_2Br—O—BrC_6H_2.CH_3$) was prepared by adding very gradually, with constant shaking, a little more than the theoretical amount of bromine to metatolyl ether dissolved in several times its weight of carbon disulphide. When the calculated amount of bromine required to form the dibromo derivative was added to the substance, *per se*, or in solution in carbon disulphide, in the dark, in direct sunlight, heated to the boiling point, at the temperature of the boiling water bath, at room temperature or at —20°, there was always formed, with equal facility, a dibromo compound which was identical in every instance. The yield was little short of quantitative. It was purified by repeated distillation, discarding the highest and lowest boiling portions each time. A portion was obtained which melted at 48°, but began to soften a few degrees lower. The substance boils at 340–350° (uncor.) under ordinary atmospheric pressure and at about 250° under 15 mm. pressure. The dibromo compound is a white, crystalline solid, which turns yellow with age. It tends to crystallize in warty aggregations on cooling from the molten state. It is soluble in carbon disulphide, alcohol, ether and several other organic solvents; sparingly soluble in absolute methyl alcohol and insoluble in water.

The substance was boiled with water and then with a strong solution of sodium hydroxide in the hope of introducing the hydroxyl group in place of the halogen atom, but without result. It was then heated in a closed tube to 200° for several hours with a strong solution of sodium hydroxide but there was no indication of any reaction. On analysis it yielded 44.55 per cent. of bromine. Calculated for $C_{14}H_{12}OBr_2$, 44.94 per cent.

*Tetrabromometatolyl ether* ($CH_3C_6H_2Br_2—O—C_6H_2Br_2.CH_3$) was found to be best prepared by adding an excess of the bromine required by calculation directly to the metatolyl ether in the presence of a little iodine and heating on the water wath to drive off the surplus bromine. The yield was very good. The substance was purified by repeated fractional distillation under diminished pressure. It boils at 260–270° under 35 mm. pressure, but decomposes when distilled under ordinary atmospheric pressure.

It is a light yellow, sticky, viscous substance, which crystallizes in warty aggregations on standing for some time. It becomes fluid on gently warming and is soluble in carbon disulphide, but is insoluble in alcohol, ether, and most common organic solvents. The compound was boiled with water, a strong solution of potassium hydroxide, and water and precipitated calcium carbonate, respectively, for some hours, without any evidence of chemical action. It was heated in a closed tube with each of these reagents for three or four hours, at 200–300°. The tube containing potassium hydroxide showed some signs of chemical action, but it was by no means complete—in fact, it was only in the initial stage. The filtrate yielded a precipitate with silver nitrate in the presence of nitric acid which was soluble in ammonium hydroxide, and a small quantity of an organic substance, presumably, a hydroxymetatolyl ether, was precipitated by neutralizing with an acid. An analysis yielded 61.85 per cent. of bromine. Calculated, 62.26 per cent.

In one experiment in the bromination of metatolyl ether, the bromine was added to the metatolyl ether, *per se*, at 150° in direct sunlight, but the bromine, as shown by various experiments, was as firmly bound as in brominating at 0°. When double the amount of bromine was added, or even a much larger excess, there was produced, with equal readiness, a tetrabromo compound under varying conditions of sunlight and darkness, heat and cold. Some of the tetrabromo compound always appeared to be formed in preparing the dibromo derivative by employing the amounts of reacting substances required by calculation, and there always remained some of the other unacted upon, but only a very small amount. The reaction was quite clear cut and the two foreign substances were readily separated from the dibromometatolyl ether by fractional distillation. In the preparation of the tetrabromo derivative by employing the amounts of the reacting substances required by calculation, there was obtained a little tar and a very little of the dibromo compound was obtained, but the reaction was far more clear cut than is usual in similar cases. It proved impossible to induce metatolyl ether to combine with more than four atoms of bromine, no matter how large an excess was added. No carrier was used in these experiments. Subsequently metatolyl ether was brominated in the presence of a little iodine in order to determine whether a higher derivative would be formed, but only the tetrabromo compound was obtained, nor did the presence of iodine seem to facilitate the reaction to any extent. It would appear, therefore, that metatolyl ether is more easily brominated than phenyl ether.

I believe, for the following reasons, that the bromine enters the nucleus and not the side chain in these experiments. The bromine derivatives effectually resisted all attempts to prepare from them compounds analogous to benzyl alcohol and benzaldehyde by all of the common methods. The bromine is very firmly linked in these compounds, and all attempts to introduce the hydroxyl group in its place were unsuccessful. This is in accordance with what would be expected if the halogen entered the nucleus. Neither of the two compounds, when purified, gave off vapors which attack the mucous membrane of the eyes, as in case of substances formed by the halogen entering the side chain, but when freshly prepared, and before purification, they did have this property, indicating the possible formation of a small quantity of the side chain compounds. Perhaps the halogen might be induced to enter the side chain by employing a still higher temperature, in direct sunlight, but the experiment was not tried on account of lack of both time and material.

The tolyl ethers are markedly different from toluene and its homologs in their action toward bromine, for in these the halogen enters the side chain in direct sunlight, or at the boiling point of toluene, and it enters the nucleus in the dark, when cold.

### 4-Methyl-2',4'-Dinitrophenyl Ether and Derivatives.

Having carried out a number of reactions between potassium phenolate and the potassium cresolates, which have been reported in this and other journals, it was thought that it might be interesting and profitable to extend the study to bromdinitro benzene.

*4-Methyl-2',4'-dinitrophenyl ether* ($CH_3C_6H_4OC_6H_3(NO_2)_2$) was prepared by mixing molecular equivalents of potassium paracresolate and 1 bromo-2,4-dinitrobenzene and warming very gently to start the reaction. (In one instance when the two reacting substances had been finely powdered and intimately mixed, the reaction took place at ordinary room temperature, with considerable rise of temperature.) When the action was well started a gentle ebullition took place, which gradually died down when the reaction was completed.

The resulting substance was dissolved in hot alcohol, filtered from the precipitated bromide, and allowed to crystallize. After three recrystallizations it melted sharply at 93°. The yield was nearly quantitative. It is a yellow-colored substance, very soluble in hot alcohol, but sparingly soluble in the cold. It is also quite soluble in various other organic solvents. Analysis for nitrogen yielded 10.64 per cent. Calculated, 10.22 per cent.

On adding a solution of sodium hydroxide to some of the substance a reaction at once set up with evolution of heat. The compound was apparently saponified with the production of paracresol and 2,4-dinitrophenol.

*The free sulphonic acid* ($(NO_2)_2C_6H_3OC_6H_3CH_3SO_3H$) was prepared by dissolving the ether in concentrated sulphuric acid, by the aid of the boiling water bath, precipitating the excess of sulphuric acid with freshly prepared lead chloride, and then precipitating the lead with hydrogen sulphide and evaporating to crystallization.

It is very soluble in water and shows a tendency to crystallize in radial aggregations of fine needles, like many other derivatives of phenyl ether.

On heating to 85° in the air bath in contact with air it melted and lost in weight corresponding to one and one-half molecules of water of crystallization. However, when heated in a melting-point tube, it did not melt until the temperature of 150° was reached and then with apparent decomposition. When a weak water solution was mixed with sodium carbonate, calcium carbonate, and barium carbonate, it caused a brisk evolution of carbon dioxide. Its water solution is only slightly yellow but a solution of the barium salt in water is quite yellow, which becomes much more intense on heating. A solution of the sodium salt is much yellower still and intensifies on warming a few degrees.

Analyses resulted as follows:

Calculated for $C_{13}H_{10}O_8S + 1^1/_2H_2O$: S, 8.4 ; $H_2O$, 9.61.
Found: S, 8.28; $H_2O$, 9.69, 9.53.

*The barium salt*, $((NO_2)_2C_6H_3OC_6H_3CH_3SO_3)_2Ba$, was prepared by dissolving the ether in concentrated sulphuric acid and diluting with a large amount of water, treating with an excess of barium carbonate to precipitate the sulphuric acid and change the sulphonic acid to the barium salt and evaporating to crystallization. Attempts to prepare the barium salt as in case of the mononitrophenyl ether, by precipitating the excess of sulphuric acid with barium chloride and then adding a sufficient amount to change the sulphonic acid to the barium salt, were unsuccessful. In attempting to crystallize the product formed, it seemed to decompose and form a compound insoluble in water.

The barium salt is light yellow in color, but when heated to 100° it assumes a much deeper tint. The water solution is much yellower than the salt itself. It is different from most of the barium salts of the sulphonic acid derivatives of the phenyl ethers thus far prepared in that it does not contain any water of crystallization.

On adding a few drops of concentrated hydrochloric acid to a solution of the barium salt, it clears up immediately, probably due to the formation of barium chloride and the liberation of the free sulphonic acid, which is nearly colorless. Two analyses yielded 16.30 and 16.29 per cent. of barium; calculated for $(CH_3.(NO_2)_2.C_7H_6OSO_3)Ba$, 16.34 per cent.

*The sodium salt* $((NO_2).C_6H_3OC_6H_3.CH_3SO_3NO)$ was prepared by precipitating the barium of the barium salt with sodium carbonate and also by neutralizing the free sulphonic acid with sodium carbonate and evaporating to crystallization in each case. When dry, the salt is light yellow in color but when moist it is brilliant yellow. Its water solution is very yellow. On adding a few drops of strong acid to a solution in water, the yellow color almost entirely disappears. It melted at 145°. On heating to 100°, it loses in weight, corresponding to one and one-half molecules of water of crystallization. On coming in contact with the air again for a few hours, it absorbs moisture from the air until it attains its original weight. An analysis resulted as follows:

Calculated for $C_{18}H_9O_8N_2SNa + 1^1/_2H_2O$: Na, 6.00; $H_2O$, 2.29.
Found: Na, 6.11; $H_2O$, 2.55.

*Other Salts.*—Attempts were made to prepare the chromium and cobalt salts by precipitating the barium from the barium salt by means of chromium sulphate and cobalt sulphate. Substances were obtained which were supposed to be the salts sought but they both decomposed on attempting to purify them by crystallization.

*2 : 4-Dinitro-p-phenoxybenzoic acid* ($(NO_2)_2.C_6H_3OC_6H_4.COOH$) was prepared by dissolving the dinitrophenylmethyl ether in glacial acetic acid and, while warming on the water bath, adding a solution of chromic anhydride in water until a test portion would yield a precipitate on addition of a large volume of water which would completely dissolve on addition of an alkali.

The acid was purified by dissolving in a dilute solution of ammonia, boiling off the excess of ammonia, precipitating the free acid again by adding hydrochloric acid and washing the precipitate free from chlorine. The acid is of a canary-yellow color. It is insoluble in water, ether, petroleum ether, methyl alcohol and benzene. It is only slightly soluble in ethyl alcohol. It did not melt when heated to 200°.

*The silver salt* ($(NO_2)_2.C_6H_3OC_6H_9.COOAg$) was prepared by precipitation by adding silver nitrate to a solution of the ammonium salt obtained as described above. It is of a canary-yellow color at ordinary temperature, but darkens when heated to 100°, but does not lose in weight. Analysis yielded 26.09 per cent. of silver. Calculated, 26.27 per cent.

Only one other of the nitrophenyl ethers heretofore prepared has yielded a carboxylic acid by oxidizing the side chain with chromic acid in acetic acid solution.

## 2,4-Dinitrophenyl Ether and Derivatives.

(The experimental work of this chapter was carried out by Mr. Carl Englund, under my direction.)

*2,4-Dinitrophenyl ether* ($C_6H_5OC_6H_3(NO_2)_2$) was prepared by grinding up in a mortar equimolecular quantities of potassium phenolate and 1,2,4-bromodinitrobenzene. A reaction began in the cold which was carried to completion by heating on a water bath. There resulted dinitrophenyl ether in the form of a brown oil and solid potassium bromide. The oil distilled without decomposition at 230–250° under a pressure of 27 mm. and solidified after standing for a short time. It was crystallized from hot alcohol several times and then melted sharply at 70°. The yield was quantitative.

2,4-Dinitrophenyl ether is very soluble in alcohol and various other organic solvents and slightly soluble in water. It has a faint odor and a burning, biting taste. An analysis for nitrogen yielded the following results: Calculated for $C_{12}H_8O_5N_2$, 10.70 per cent; found, 10.75 per cent.

Attempts to reduce the nitro groups with tin and hydrochloric acid were unsuccessful. The base decomposed immediately on exposure to the air.

Some of the 2,4-dinitrophenyl ether was heated with water at 100° for several hours in closed tubes with the idea of hydrolyzing the substance, but without effect. However, when heated under the same conditions with sodium hydroxide, chemical reaction had taken place. The tube was filled with ammonia gas and crystals of a foreign substance were deposited on standing. On account of lack of time, however, they were not studied farther.

*2,4-Dinitrophenylethersulphonic acid* ($(NO_2)_2.C_6H_3OC_6H_4.SO_3H$) was prepared by gently warming 2,4-dinitrophenyl ether with concentrated sulphuric acid. It yielded a solution which was not precipitated by the addition of water. The excess of sulphuric acid was precipitated by the addition of barium chloride. On evaporating the filtrate on the water bath, the sulphonic acid was obtained in the form of pearly white flakes. It is easily soluble in water and has a strong, bitter taste much like picric acid.

The analysis for sulphur (though now lost) yielded results which corresponded with the requirements of theory.

*The barium salt* ($((NO_2)_2C_6H_3OC_6H_4.SO_3)_2Ba + {}^1/_2H_2O$) of the sulphonic acid was obtained by adding an excess of barium chloride to the solution of the sulphonic acid in dilute sulphuric acid, obtained as described above. On evaporating over the water bath, the barium salt of the sulphonic acid was obtained in the form of pearly flakes which do not melt without decomposition. It is difficultly soluble in cold water but readily soluble in hot water. On heating in the air bath to 200°, it lost in weight corresponding to one-half molecule of water of crystallization. Two analyses for barium yielded 16.93 per cent. and 16.86 per cent., respectively. Required by calculation, 16.85 per cent.

Several unsuccessful attempts were made to prepare other salts. Strontium carbonate, copper carbonate, and potassium carbonate were added to solutions of the pure sulphonic acid, and although effervescence took place in each case, no well defined salts were isolated.

*Trinitrophenyl ether*, $C_{12}H_7O(NO_2)_3$, was obtained by dissolving the dinitrophenyl ether in strong nitric acid. On pouring this mixture into water, there was precipitated a gummy mass, which solidified on rubbing up with cold water. It was crystallized from methyl alcohol and obtained in the form of warty masses and radiating clusters of yellow prismatic crystals. Two analyses yielded 14.29 and 14.23 per cent., respectively, of nitrogen. Calculation requires 13.77 per cent.

## Bibliography.

(1) *Ann.*, **90**, 209.—List and Limpricht obtained diphenyl ether as one of the products of the destructive distillation of copper benzoate. (2) *Ann.*, **125**, 328.—Rudolph Fittig obtained diphenyl from the above-mentioned distillate. (3) *Ann.* **138**, 375.—C. Lesimple obtained a compound by distilling phenyl phosphate with lime, which he called phenyl ether. (4) *Ann.*, **159**, 191, and *Ber.*, **3**, 747.—W. Hoffmeister prepared phenyl ether by treating diazobenzene sulphate with phenol and made a thorough study of the compound. (5) *Ber.*, **23**, 3709.—Hirsch varied Hoffmeister's method and greatly increased the yield. (6) *Ber.*, **6**, 564.—Maikopar made a dinitro derivative by acting on dinitrochlorobenzene with an alcoholic solution of potassium hydroxide and phenol. (7) *Ber.*, **12**, 762.—Willgerodt prepared a dinitrophenyl ether by the above method. (8) *Ber.*, **12**, 1277.—Willgerodt prepared a trinitrophenyl ether by the same method. (9) *Ber.*, **13**, 887.—Willgerodt prepared a tetranitro derivative by heating dinitropotassium phenolate with dinitrochlorobenzene in a sealed tube. (10) *Ber.*, 14, 187.—Merz and Weith prepared phenyl ether by heating phenol with zinc chloride, and also aluminium chloride (see also correspondence, *Ber.* **12**, 1925). (11) *Ber.*, **15**, 1123.—Niederhausern prepared methylene diphenyl oxide by distilling sodium phenolate with sodium metaphosphate. (12) *Ber.*, **17**, 1764.—Willgerodt and Huetlin prepared derivatives by acting on potassium phenolates with dinitrochlorobenzene and picryl chloride. (13) *Ber.*, **17**, 2638.—Bausch prepared a dimethyl derivative by heating paracresol with zinc chloride. (14) *Ber.*, **29**, 1446.—Haeussermann and Teichman prepared various derivatives by acting on halogen nitrobenzene derivatives with potassium of sodium phenolates. (15) *Ber.*, **29**, 1878.—F. Ullman, independently, from the above-mentioned investigators, made a few compounds by the same method. (16) *Ber.*, **29**, 2083, and *Ibid.*, 30, 738.—Hauessermann and Bauer continued the work begun by Haeussermann and Teichman and prepared numerous compounds. (17) *J. Chem. Soc.*, **41**, 5, and *Ibid.*, 49, 27.—Gladstone and Tribe prepared phenyl ether and derivatives by distilling aluminium phenolate, aluminium thymolate, and aluminium cresolates. (18) *Chem. News*, **42**, 3.—See No. 15 above. (19) *Chem. News*, **42**, 146.—See No. 8 above. (20) *J. prakt. Chem.*, 1, 143.—See No. 4 above. (21) *J. prakt. Chem.*, (2) **28**, 273.—Klepl prepared carbonyl phenyl oxide by the action of triphenyl phosphate on sodium salicylate. (22) *J. prakt. Chem.*, (2 **28**, 193.—Klepl prepared phenyl ether by distilling paraphenoxybenzoic acid with caustic baryta. (23) *J. prakt. Chem.*, (2) **28**, 201.—Richter prepared diphenyl oxide by distilling sodium salicylate and triphenyl phosphate. (24) *Monatshefte*, **17**, 65.—B. Jeitles distilled calcium phenyl phosphate and obtained, among other things, diphenyl ether. (25) *Gazetta*, 28, (1) 197.—G. Ortoleva and A. Paratoner treated diphenyl ether with sulphonyl chloride and obtained chlorine derivatives. (Abstract in *J. Chem. Soc.*, 1898.) (26) *Am. Chem. J.*, **24**, 525.—Cook and Hillyer prepared 2-nitro-4′-methylphenyl ether and several derivatives. (27) THIS JOURNAL, **23**, 806.—Cook prepared 2-nitro-2′-methylphenyl ether and several derivatives. (28) THIS JOURNAL, **24**, 1200.—Cook and Eberly prepared 4-nitro-2′-methylphenyl ether and various derivatives. (29) *Am. Chem. J.*, 28, 486.—Cook and Frary prepared 4-nitro-3′-methylphenyl ether and various derivatives. (30) THIS JOURNAL, **25**, 60.—Cook prepared 4-nitro-4′-methylphenyl ether and various derivatives. (31) THIS JOURNAL, **26**, 302.—Cook described the properties of phenyl ether. (32) Proceedings of the Iowa Academy of Sciences, 10, 116.—Cook made a study of the Hirsch-Hoffmeister method of preparing phenyl ether. (33) *Ber.*, **37**, 853.—Ullman prepared phenoxybenzoic acid by heating orthochlorobenzoic acid with potassium phenolate in the presence of copper. (34) *Ber.*, **32**, 2211.—Ullman and Sponagle prepared phenyl ether by the above-mentioned method. (35) *Ann.*, **350**, 83.—Ullman and

Sponagle prepared various methylphenyl ethers, using copper as a catalytic agent. (36) THIS JOURNAL, 28, 608.—Cook studied aluminium phenolate with reference to the preparation of phenyl ether. (37) *Ber.*, 38, 2490.—Kipper prepared several derivatives of phenyl ether by means of Friedel and Crafts' reaction. (38) *Am. Chem. J.*, 36, 543.—Cook prepared metatolyl ether and several of its derivatives.

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# THE STEREOMERIC AZOBENZENES.

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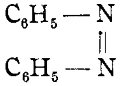
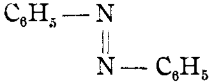
## Introduction.

It is apparent from the structural formula of azobenzene that two stereomeric modifications should exist, one in which both aromatic nuclei are on the same side of the nitrogen bridge or *syn*-azobenzene (I), and the other where the nuclei are opposite each other or *anti*-azobenzene (II):



$$\begin{array}{r} C_6H_5 - N \\ \| \\ C_6H_5 - N \end{array}$$

(I)



$$\begin{array}{l} C_6H_5 - N \\ \qquad\quad\;\; \| \\ \qquad\quad\;\; N - C_6H_5 \end{array}$$

(II)

Although many such examples of syn and anti forms are known in the diazo compounds,[1] the authors are not aware of any such isomerism having been observed in the azo group.

Some years ago one of us had occasion to prepare azobenzene during a course in "organic preparations," but could not by any means obtain a compound melting at 68°, the melting point of azobenzene as described in the literature. Crystals were, however, obtained which melted at "about 23°," as the notes were then recorded. It afterward seemed probable that this was the unknown stereomeric form and we have recently taken up the subject again, obtaining results which lead us to believe that such was the case.

## Experimental.

The azobenzene was produced by the dry distillation of azoxybenzene and clean iron filings from a small non-tubulated retort. The azoxybenzene was prepared according to the method of Lachman.[2]

Thirty grams of nitrobenzene were added to 250 cc. of methyl alcohol containing 40 grams of sodium hydroxide and the mixture heated during three hours on an actively boiling water bath. The methyl alcohol was then distilled off and the residue poured into ice-water. The azoxybenzene separated as an oil which soon became solid. This solid was well washed, melted with dilute hydrochloric acid to remove traces of aniline, washed free of acid, and recrystallized from 90 per cent. alco-

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[1] Holleman, "Lehrb. d. Organ. Chem.," Leipzig, 1908, p. 362.

[2] THIS JOURNAL, 24, 1178 (1902).