

with absolute alcoholic potash until the solution was faintly alkaline. The potassium chloride was filtered off and the filtrate evaporated to dryness. The base was purified by crystallization from aqueous acetone, out of which it separated in cubes which melted at 270°. It is soluble in water and alcohol and insoluble in acetone and ether. Unlike cytosine, this base is not hydrated. It gives the Wheeler-Johnson color test.³

Anal. Calcd. for C₈H₇N₃O: N, 33.60. Found: N, 33.38, 33.30.

The picrate of 2-oxy-6-methylaminopyrimidine crystallizes from water in slender prisms and melts at 220–225°.

Summary

1. The interaction of methylamine and 2-ethylmercapto-6-chloropyrimidine produces either 2-ethylmercapto-6-methylaminopyrimidine or 2,6-di-(methylamino)-pyrimidine, depending on the temperature employed.

2. A new methylcytosine, 2-oxy-6-methylaminopyrimidine, is formed by acid hydrolysis of 2-ethylmercapto-6-methylaminopyrimidine.

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

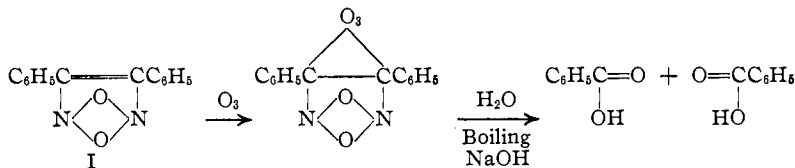
THE STRUCTURE OF FURAZAN OXIDES. II

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Furazan oxides (or furoxans) are attacked by ozone and the ozonized substances are decomposed with water and alkalis yielding acids. This behavior of these substances has been interpreted¹ on the basis of an ethylenic structure as follows



Meisenheimer, Lange and Lamparter,² however, have succeeded in isolating two substances which they believe to be isomeric furazan oxides. The isolation of two isomeric oxides does not permit an ethylenic formula, I, but necessitates an unsymmetrical structure, which in the case of Meisenheimer's oxides would have Formulas II and III.



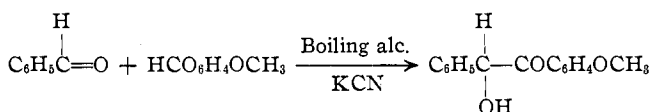
The two isomeric oxides II and III were obtained by oxidizing the two *amphi*-dioximes of *p*-methoxybenzil. They appeared to be non-separable and isomorphous since recrystallization of a mixture from alcohol did not

¹ Kinney and Harwood, *THIS JOURNAL*, **49**, 514 (1927).

² Meisenheimer, Lange and Lamparter, *Ann.*, **444**, 94 (1925).

seem to change the melting point; the melting points of various mixtures was not lowered, but fell between the two extremes. In order to elucidate the mechanism of the reaction of furazan oxides with ozone, a study of Meisenheimer's two oxides has been made in this Laboratory and new and more convenient syntheses of these substances and of the oximes from which they are made developed.

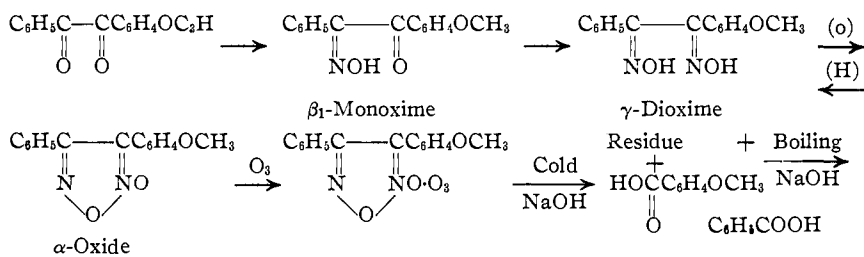
Benzaldehyde and anisaldehyde have been condensed together to form *p*-methoxy-benzoin,^{2a} but we are aware of no case in which an attempt has been made to condense the two aldehydes in satisfactory yields. The condensation takes place readily with the anisaldehyde adding to the benzaldehyde. This manner of reaction



is undoubtedly due to the difference in reactivity of the two carbonyl groups. Difficulty was experienced in oxidizing the benzoin derivative to *p*-methoxybenzil using the old nitric acid process for benzil, but the method outlined in "Organic Syntheses"³ is to be highly recommended for *p*-methoxybenzil.

The earlier synthesis of the two oxides of phenyl-*p*-methoxyphenyl-furazan involved the preparation of the two *amphi*-dioximes of *p*-methoxybenzil, which in turn were made from the two β -monoximes. When *p*-methoxybenzil was heated with one equivalent of hydroxylamine, the β_1 -monoxime⁴ was the exclusive product, due again to the difference in reactivity of the carbonyl groups. This prevented the direct synthesis of the α -dioxime and the β - or lower melting oxide, III; in order to synthesize this isomer we used two other methods.

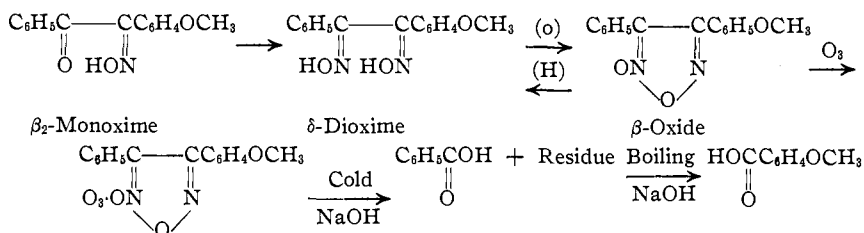
Both carbonyl groups of *p*-methoxybenzil were oximated at once and the resulting product, which was largely the β -dioxime, was oxidized to a mixture of the α - and β -oxides. By means of persistent fractional



^{2a} Ekecrantz and Ahlquist, *Arkiv. Kem. Min. Geol.*, **3**, (No. 13) 1-26 (1908). See also Staudinger, *Ber.*, **46**, 3535 (1913).

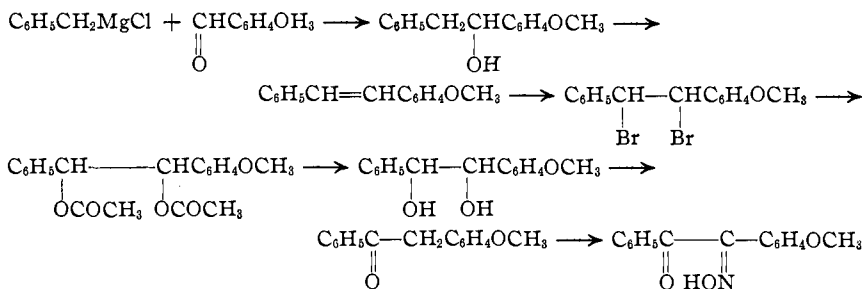
³ "Organic Syntheses," John Wiley and Sons, Inc., New York, **6**, 6 (1926).

⁴ We will use Meisenheimer's system of nomenclature.



crystallization from acetone (instead of alcohol) the two oxides were separated. About one-tenth of the product was the β -oxide.

The second method involved the synthesis of the β_2 -monoxime from phenylanisyl ketone, in the following way. Owing to repeated small yields this method has little to recommend it over the above or over Meisen-



heimer's synthesis which involved *p*-methoxyphenylnitromethane as a starting material.

In general we have found the work of Meisenheimer, Lange and Lamparter on the oximes and oxides of the *p*-methoxy series to be quite correct except for the purity of the two oxides. By repeated recrystallizations from acetone (instead of alcohol, in which these substances are fairly insoluble cold) the α -oxide was found to melt at 108–109° and in like manner the melting point of the β -isomer was raised to 104–105° with softening at 102°. The β -oxide probably was not perfectly pure even then but was sufficiently so for most purposes. The melting point of mixtures of the two purified oxides were always lower, the eutectic point being the 95–97° mixture of Meisenheimer and designated by him as the β -isomer. The two substances behave similarly chemically and are undoubtedly the isomeric furazan oxides, II and III.

The appearance of two isomeric furazan oxides disproved the ethylenic structure, I, and demands an unsymmetrical formula such as II and III. On this basis the attack of these substances by ozone cannot be explained by means of an ethylenic linkage. The imino linkage did not react with ozone in the aromatic furazans (or oxazoles). Diphenylfurazan when treated with ozone reacted slowly and did not produce acids as did the furazan oxides. The only remaining point of attack was the side of the

molecule holding the extranuclear oxygen atom, that is, the NO linkage or an endoxy linkage if that be preferred. Since carbonyl groups add on ozone, it seems possible that the NO linkage would react likewise, followed by a stepwise decomposition of the molecule.

The two isomeric oxides of phenyl-*p*-methoxyphenylfurazan reacted with ozone in the same way as the diphenyl derivative.¹ Upon decomposition with cold sodium hydroxide the α -isomer yielded anisic acid while the β - produced benzoic acid. The residue from the α -, when boiled with sodium hydroxide, yielded largely benzoic acid and the residue from the β - largely anisic acid (see diagram, pp. 1593-1594). The structural difference between the two oxides is thus clearly demonstrated.

The process of oxidation has been shown to start on the side of oxidized nitrogen and to instigate a stepwise decomposition of the molecule. The aromatic group nearer the point of attack would be the first to appear as aromatic acid and the one farther removed to appear after boiling with sodium hydroxide. All of this may be used for determining which structure to give to the individual oxides and to the dioximes from which they are obtained and into which they may be transformed.

Meisenheimer based the structures of the oximes given in the diagram largely upon his work with triphenylisoxazole and ozone;⁵ they are the reverse as determined by the Beckmann rearrangement. The furazan oxides obtained from the α - and β -dioximes by oxidation were given structures by him corresponding to the dioxime from which they were obtained. By means of our reaction with ozone the structures assigned to the oxides by Meisenheimer must be correct, since the process of ozonization and decomposition with alkali requires that the extranuclear oxygen atom be attached nearer the *p*-methoxyphenyl in the α - or higher melting isomer and nearest the phenyl group in the β -, as shown in the diagram. Thus we have proof from a still different source as to the correctness of the configuration of the dioximes as set forth by Meisenheimer.

Experimental Part

p-Methoxybenzoin.⁶—Since benzaldehyde condenses in the presence of potassium cyanide much more rapidly than anisaldehyde, we allowed benzaldehyde, in our earlier experiments, to drop slowly into a boiling alcoholic solution of anisaldehyde and potassium cyanide. This procedure was found to be unnecessary and as good yields were obtained by mixing the aldehydes at the outset. The following was our best practice.

Fifty grams of potassium cyanide was dissolved in 350 cc. of water in a 3-liter flask. To this was added 272 g. (2 moles) of anisaldehyde,⁷ 212 g. (2 moles) of benzal-

⁵ Meisenheimer, *Ber.*, **54**, 3206 (1921); see also Köhler and Richtmyer, *This Journal*, **50**, 3105 (1928).

⁶ Obtained in another way by Meisenheimer with Jochelson, *Ann.*, **355**, 249-311 (1907).

⁷ No particular advantage was noticed with redistilled aldehydes and in most of our work Eastman's "Practical" grade was used.

dehyde⁷ and 700 cc. of 95% alcohol. The mixture formed a solution at the boiling temperature and was refluxed for one and one-half hours. Steam was then passed through the solution until all of the alcohol and nearly all of the unchanged aldehydes were removed. The condensed water was decanted from the product and the latter set away to crystallize. The product was then pressed as free as possible from oily material on a suction funnel and washed with cold alcohol. In this way about 250 g. of crude product was obtained. The crude mixture was dissolved in hot alcohol and allowed to crystallize slowly. The *p*-methoxybenzoin crystallized out first in large clumps of long needles, while the benzoin crystallized in small compact balls of needles. With some experience a good yield of nearly pure *p*-methoxybenzoin can be filtered out before the appearance of the benzoin. The yield of pure *p*-methoxybenzoin amounted to 100–110 g. For conversion into *p*-methoxybenzil only two or three recrystallizations were necessary, or until the melting point reached 102 or 103°.

***p*-Methoxybenzil.**—The usual method for making benzil from benzoin by nitric acid oxidation was not applicable to the oxidation of *p*-methoxybenzoin. The oxidation proceeded too far and considerable oily material made a separation of the benzil derivative impractical. However, the method described in "Organic Syntheses"⁸ gave an 85 to 90% yield. The procedure followed in isolating the derivative was slightly different from that given there. After the oxidation had proceeded for two hours and the pyridine-copper sulfate solution was dark green in color, the mixture was transferred while still hot to a separatory funnel and the pyridine-copper sulfate solution drawn off. Ether and 10% hydrochloric acid were then added and the mixture shaken until the odor of pyridine had disappeared. After separation of the acid layer the ether solution was partially evaporated and alcohol and water added. The substance crystallizes readily when fairly pure in spite of its low melting point. It is best recrystallized from about 80% alcohol; m. p. 62–63°; bright yellow in color.

*Anal.*⁸ Subs., 0.2013: H₂O, 0.0886; CO₂, 0.5783. Calcd. for C₁₅H₁₄O₃: C, 75.0; H, 5.0. Found: C, 75.0; H, 5.04.

The γ -Dioxime of *p*-Methoxybenzil and the Preparation of the α -Oxide of Phenyl-*p*-methoxyphenylfuran.⁹—Meisenheimer, Lange and Lamparter² synthesized the β -monoxime of *p*-methoxybenzil by means of a rather long and laborious process. We found that *p*-methoxybenzil was readily changed to the above oxime in the following way.

Forty grams of *p*-methoxybenzil and slightly less than one equivalent of hydroxylamine hydrochloride were dissolved in a minimum of alcohol and refluxed for one and a half hours. The solution was then poured into water and the oxime extracted with benzene. The benzene solution was extracted with 10% sodium hydroxide and the oxime precipitated with carbon dioxide. After one crystallization from benzene the melting point was 120–124° but after two recrystallizations from carbon disulfide it was raised to 129–130°. The yield was 25 g.

Three or four grams of unchanged ketone was recovered, but no β_2 -monoxime. The remainder of the product did not crystallize.

The preparation and properties of the γ -dioxime and the α -oxide prepared from it are correct as given by Meisenheimer except for the melting point of the latter substance which is discussed in detail under the separation of the oxides on page 1597.

The Preparation of the Mixed Oxides of Phenyl-*p*-methoxyphenylfuran.—The oxidation of either the α - or β -dioxime of *p*-methoxybenzil yields a mixture of the two oxides of phenyl-*p*-methoxyphenylfuran.² However, several attempts to prepare the α -dioxime using the method for making the α -dioxime of benzil resulted in poor

⁸ By Marcel Mayhue.

⁹ By G. E. Hinckley.

yields, but the α -dioxime obtained had the melting point given by Meisenheimer and not that of the product obtained by Ponzio¹⁰ in an entirely different manner.

Also, attempts were made to oximate the ketone using pyridine solutions. The color of the ketone was rapidly discharged, but the separation of the reaction products was not very successful. This method of oximation appeared worthy of further investigation.

Our best method for getting a dioxime for oxidation to the oxides was as follows. Twenty-four grams (0.1 mole) of *p*-methoxybenzil was dissolved in 50 cc. of alcohol, 7 g. (0.1 mole) of hydroxylamine hydrochloride dissolved in 10 cc. of water added and the whole refluxed for thirty minutes. Then 10.5 g. (0.15 mole) of hydroxylamine hydrochloride in 10 cc. of water, 15 cc. of 6 *N* sodium hydroxide and 35 cc. of alcohol were added and the whole boiled for forty-five minutes. Finally, 30 cc. of 6 *N* sodium hydroxide was added and the solution refluxed for one hour and forty-five minutes. At the end of this time the solution was diluted with a liter of water and an insoluble precipitate, probably of the furazan, filtered out. Dilute acid was added to precipitate the oximes, which were separated by decanting the water from the sticky product. The oximes were dissolved in 300 cc. of 6 *N* sodium hydroxide and diluted to 4 liters. Sodium hypochlorite made from 10% sodium hydroxide and chlorine was added to the above solution (cooled by addition of ice) until no more precipitation occurred. The precipitated oxides were recrystallized from acetone and petroleum ether (or alcohol). The first crop weighed 12.7 g. (m. p. 99–102°); the second, 1.5 g. (m. p. 93–95°); the third, 0.6 g. (somewhat oily).

The preparation of the dioximes can undoubtedly be improved considerably. Too early addition of sodium hydroxide cut the above yield in half. Also, the oxidation of the dioxime should not be carried out before precipitating out the oxime from the solution containing hydroxylamine. Considerable material was lost earlier in this way, as a rather strange decomposition took place. The precipitate when allowed to warm up turned green, evolved gas and finally turned into a yellow-orange liquid product. Anisic acid was formed simultaneously.

The Separation of the Phenyl-*p*-methoxyphenylfurazan Oxides.—Eighty-three grams of the mixed oxides obtained much as described above was fractionally crystallized from acetone and a mixture of acetone and petroleum ether. The higher melting oxide crystallized first in considerable quantities and relatively pure (m. p. 102–105°). Repeated fractions were necessary to isolate the 95–97° mixture of Meisenheimer and to isolate a higher melting product which when mixed with the α -oxide was lowered. The mixed oxides were finally separated into fractions of 58 g. of the α -oxide and 8.6 g. of lower melting β -oxide. The α -oxide after repeated recrystallizations finally melted at 108–109°. The 8.6 g. of impure β -oxide upon further fractionation yielded 4 g. of oxide melting at 104–105° with softening at 102°. This was probably not perfectly pure even then since it softened below the melting point and since the products of oxidation with ozone were not as clean as with the α -oxide.

The relatively smaller yield of the β -oxide from the β -dioxime is difficult to explain since the mechanism of the process by which the oximes are transformed into the furazan oxides is obscure. However, it seems likely that the two hydrogen atoms of the oximino groups (or, if the oxidation is carried out in an alkaline solution, the two ionic charges) are removed, leaving an unstable arrangement which at once changes into the furazan oxide. In the case of the β -dioxime the influence of the *p*-methoxyphenyl group apparently shows up in the amounts of the two isomers actually formed. The yield of the β -oxide from the α -dioxime may be greater, but we have not tried this because of insufficient quantities of the α -dioxime.

¹⁰ Ponzio and Bernardi, *Gazz. chim. ital.*, **53**, 813 (1923).

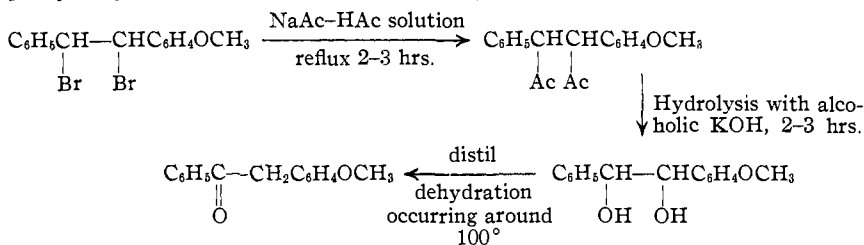
The Second Method for Preparing the β -Oxide and the Ozonization of Diphenyl Furazan¹¹

p-Methoxyphenylbenzylcarbinol and *p*-Methoxystilbene.—*p*-Methoxyphenylbenzylcarbinol¹² was prepared using the Grignard reaction in the usual way. This compound has since been described in the literature and consequently will not be described here; however, we have analyses and molecular weight determination which are in good agreement. It is best recrystallized from ether and petroleum ether.

For our purpose of preparing *p*-methoxystilbene we did not attempt to isolate the carbinol in our later experiments, but simply distilled the crude reaction product under a water-pump vacuum. A yield of 90% of *p*-methoxystilbene is obtained from anisaldehyde in this way.

p-Methoxystilbene Dibromide.—Our best yield of dibromide was only 78% and often yields were much poorer. Better yields were obtained by cooling and stirring the reaction mixture (a chloroform solution was used) and by slow addition of bromine. The insoluble dibromide was purified by washing with ether.

p-Methoxydisoxybenzoin.—The *p*-methoxystilbene dibromide was changed into phenylanisyl ketone, $C_6H_5COCH_2C_6H_4OCH_3$, by the following reactions



No attempts were made to isolate intermediate substances. The diacetate was obtained from the acetic acid solution by diluting with water and decanting the solution from the sticky acetate. The mixed hydrobenzoin was obtained from the alcoholic solution in much the same way except that it was collected and introduced into the distilling flask using ether as a solvent. The yields were 30-40%.

β_2 -Monoxime of *p*-Methoxybenzil.—Nine grams of phenylanisyl ketone was dissolved in 50 cc. of dry alcohol and 10 cc. of sodium ethylate solution, prepared from 1 g. of sodium, added. To this solution cooled to 0° was slowly added 7 g. of amyl nitrite. The orange-colored solution was set away in a cool place for twenty-four hours. The oxime was then extracted with 10% sodium hydroxide solution and precipitated by passing carbon dioxide into the solution until saturated.

The oxime was purified by solution in 10% sodium hydroxide and reprecipitation with carbon dioxide, followed by recrystallization from hot alcohol. The yield was 3.5 g. or 36% and the melting point 169-170°. Considerable amounts of *p*-methoxystilbene appeared at this point, probably coming from a different dehydration process than the one outlined for the hydrobenzoin; that is, our phenylanisyl ketone was not perfectly pure.

The Change of the β_2 -Monoxime into the β -Oxide.—The δ -dioxime of *p*-methoxybenzil is not very stable and the purification is complicated because of its tendency to form compounds with molecules of the solvent of crystallization. Consequently in

¹¹ By H. J. Harwood.

¹² The general method for preparing *p*-methoxydesoxybenzoin or phenylanisyl ketone was that as outlined in *C. A.*, 20, 2324 (1926); abstract of a paper by Orekhoff and Tiffeneau, *Bull. soc. chim.*, 37, 1410-1420 (1925).

our work we usually oxidized the freshly prepared crude δ -dioxime, prepared according to Meisenheimer, Lange and Lamparter.² It seemed advantageous to precipitate the dioxime either with very dilute sulfuric acid or by adding sodium bicarbonate and then redissolve the oxime in fresh 10% sodium hydroxide and proceed with the oxidation according to Meisenheimer. The product melted at 95–97° when recrystallized from alcohol. Several recrystallizations from alcohol, in which it is fairly insoluble when cold, did not change the melting point. However, carefully repeated fractionations from other solvents does change the melting point as described under the fractionation of the mixed oxides.

The Ozonization of Diphenylfurazan.—One gram of diphenylfurazan was ozonized in nearly the same manner as diphenylfurazan oxide in the earlier experiments. Since the ozonizer was giving about 4% ozone instead of 3% as formerly, the furazan was ozonized for six hours instead of seven. When treated with sodium hydroxide in the same way as the corresponding oxide, not a trace of benzoic acid was obtained and 0.72 g. of the unchanged furazan was recovered.

The Ozonization of the Oxides of Phenyl-*p*-Methoxyphenylfurazan.—The ozonization of the oxides of *p*-methoxydiphenylfurazan was carried out as before in pure dry carbon tetrachloride as a solvent. The presence of a drop of water did not materially alter the process of oxidation, although it slowed down the rate. One-gram samples were used and a stream of ozonized oxygen containing 3–4% of ozone was passed through for nine to twelve hours. Usually, after running the ozone for about six hours the solutions stood about twenty hours (overnight) and then ozone was passed through for three to six hours more. This procedure, of course, materially lengthened the time the oxides were in contact with the ozone.

A non-explosive, sticky yellow product separated in each case after six hours' running, which could not be purified even when larger runs were made. Starting with diphenylfurazan oxide only benzoic acid could be isolated from the insoluble substance. In contact with alkalis it turned red and slowly dissolved. From the alkaline solution only benzoic acid could be obtained.

In ozonizing the *p*-methoxydiphenylfurazan oxides no attempt was made to work with the insoluble product, but 10% sodium hydroxide was added at once and the whole shaken until the ozonides had dissolved, forming a red solution. The carbon tetrachloride solution was extracted a second time with a little sodium hydroxide and finally the mixed sodium hydroxide solutions were extracted with ether and acidified. In order to ascertain the total amount of acid product, especially where benzoic acid was concerned, the acidified solution was extracted with ether two or three times. After evaporating the ether the crude acid yield was determined. The kind of acids present was ascertained by recrystallization from hot water.

The carbon tetrachloride solution above was next evaporated to a yellow liquid, which was dissolved in alcohol containing some 10% sodium hydroxide. The solution became red and after boiling for thirty minutes was diluted with water and the water extracted with ether. The water solution was acidified, extracted and the amount and kind of acid present determined as before. The residue after the extraction with boiling alcoholic sodium hydroxide was small, usually about 0.1 g. and was not the unchanged oxide.

One gram of the α -oxide after ozonization and extraction with cold 10% sodium hydroxide yielded from 0.5 to 0.6 g. of crude anisic acid. After one crystallization from hot water the acid melted at 163–164°. A second crystallization raised the melting point to 173–176°, the product still retaining some color. In a mixed melting point with an authentic specimen of anisic acid the melting point rose to 179–180°. The weight of crude acid after boiling with sodium hydroxide varied from 0.35 to 0.43 g.

Upon crystallization from hot water the melting point was 115–118° and a mixture with benzoic acid melted at 118–119°.

One gram of the β -oxide yielded after the first treatment 0.35 g. of acid. The acid was dissolved in boiling water and after cooling slightly deposited a few crystals of anisic acid. The next crop was 0.1 g. of impure benzoic acid melting at 90–95°, while remaining in solution was fairly pure benzoic acid as determined by extraction and crystallization from a smaller volume of water. Thus the crude acid was found to be largely benzoic acid.

After boiling the residue with alcoholic potassium hydroxide for one and a half hours, 0.8 g. of crude acid was obtained. The crude acid was heated with water and 0.2 g. failed to dissolve. From the water 0.5 g. of impure anisic acid was obtained, m. p. 140–50°. Recrystallization and mixed melting point determinations showed it to be anisic acid. The remaining 0.2 g. in solution was impure benzoic acid.

The Action of the Grignard Reagent on the Oxides of Phenyl-*p*-methoxyphenyl-furazan.—Phenylmagnesium bromide in excess reacted readily with the furazan oxides, the experiments of Wieland and Semper¹³ notwithstanding. Considerable heat was evolved when the reaction with diphenylfurazan oxide was allowed to proceed without cooling. There was no apparent reaction for some time, but in the end it became violent, distilling out the ether and leaving a very tarry residue. The oxides were entirely altered by allowing them to stand for two or three hours with phenylmagnesium bromide cooled with ice water. Phenol and diphenyl appeared in relatively large amounts. The quantities of these products did not vary greatly whether the reaction mixture was kept cold, refluxed after addition of the oxide or the oxide added to a boiling benzene solution of phenylmagnesium bromide. The amount of diphenyl was usually about one-half mole per mole of oxide and the amount of phenol isolated as tribromophenol between one-half and one mole. By boiling the Grignard product with alcoholic potassium hydroxide, ammonia was evolved and a semi-solid acid fraction obtained which smelled of benzoic acid. The residue from this treatment when boiled with hydroxylamine and alcoholic potassium hydroxide yielded small amounts of oximes of the type of benzophenone-oxime.

Many attempts were made to get a reaction with the oxides of phenyl-*p*-methoxyphenylfurazan and phenylmagnesium bromide in a way that would show up their differences in structure. They both yield phenol and diphenyl, but mixtures of benzophenone-oxime and probably *p*-methoxybenzophenone-oxime were obtained. This was to be expected to a certain extent from the work of Angeli¹⁴ and Bigiavi.¹⁵

Summary

A study of the isomeric oxides of phenyl-*p*-methoxyphenylfurazan has been made. It has been shown that the two substances are not isomorphous. The structural difference between them has been clearly demonstrated by the reaction with ozone followed by a stepwise decomposition. The determination of the individual structures of the oxides by means of the ozone reaction gives further proof that the configurations of the oximes, to which the oxides are closely related, are correct as set forth by Meisenheimer.

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¹³ Wieland and Semper, *Ann.*, **358**, 36 (1908); see also Wieland, *ibid.*, **424**, 107 (1921).

¹⁴ Angeli, *Gazz. chim. ital.*, **46**, 300 (1916); *Atti Accad. Lincei*, (V) **25** [2] 7 (1916).

¹⁵ Bigiavi, *Gazz. chim. ital.*, [2] **51**, 324 (1921).