[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE STATE COLLEGE OF WASHINGTON]

SOME ALKOXY DERIVATIVES OF DIPHENYL OXIDE

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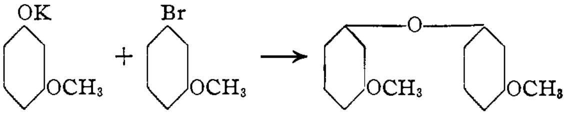
Since the stability of diphenyl oxide in the presence of alkalies has rendered compounds of this character valuable in soap perfumery, it seemed of interest to study the effect of substituents and especially of alkoxy groups on the properties of the compounds.

Ullmann and his co-workers[2] prepared diphenyl oxide by condensation of bromobenzene with potassium phenoxide, which required a temperature of 180–210° for a period of twelve hours. They found that by this method the yield was only 9% of the theoretical, but if a small quantity of metallic copper was used as catalyst, they were able to obtain a yield of 87%. *o*-Methoxy compounds were prepared by the same method.

Sabatier and Mailhe[3] prepared some mixed aryl ethers by the use of thorium oxide as catalyst. Weston and Adkins[4] prepared diphenyl oxide by treating phenol with metallic potassium and adding bromobenzene in the presence of a copper catalyst, heating the mixture to 210° for two hours.

The preparation of *m*-methoxydiphenyl oxides presented difficulties, as some of the intermediate compounds were not easily obtainable and did not condense as readily as the ortho or para compounds. In preparing the *m*-bromomethoxy and ethoxy compounds, preparatory to their condensation with alkoxy phenols to form the diphenyl oxides, the following steps were involved: nitrobenzene ⟶ *m*-bromonitrobenzene ⟶ *m*-bromoaniline ⟶ *m*-bromophenyldiazonium sulfate ⟶ *m*-bromophenol ⟶ *m*-methoxybromophenol. Phenols of the latter type were condensed with *m*-alkoxyphenols, which were prepared by the partial alkylation of resorcinol. The condensation apparently occurred as follows



A number of catalysts were used in attempts to improve the yield, under varying conditions of temperature and time, and optimum results obtained by the methods described.

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[1] Abstracted by C. M. Brewster from the thesis submitted by C. A. Doran to the State College of Washington in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

[2] Ullmann and Sponagel, *Ber.*, **38**, 2211 (1905); *J. Chem. Soc.*, **92**, 38 (1907); Ullmann and Stein, *Ber.*, **39**, 622 (1906).

[3] Sabatier and Mailhe, *Compt. rend.*, **155**, 260 (1913).

[4] Weston and Adkins, THIS JOURNAL, **50**, 859 (1928).

Experimental Part

Choice of Catalysts.—Attempts were made to prepare the diphenyl oxide derivatives by the condensation of two phenols having other groups in meta position. While it was possible to prepare diphenyl oxide from phenol using aluminum chloride as catalyst, no condensation took place when the *m*-alkoxyphenols were used. When metallic potassium was used with *m*-methoxyphenol, and the resulting salt refluxed with *m*-methoxybromobenzene in the presence of finely divided freshly reduced copper, only a trace of a high-boiling product resulted. Substitution of metallic sodium gave no better results, and in both cases a large amount of charring took place during addition of the metal to the phenol. Trials were also made with zinc chloride, concentrated sulfuric acid and freshly prepared thorium oxide on the mixed phenols, at temperatures ranging from 200 to 350°, but in no case did appreciable condensation take place. The most satisfactory method proved to be the condensation of potassium salts of phenols with the aryl halides at high temperatures, in the presence of finely divided freshly reduced copper as catalyst. This method gave fair results with bromo-alkoxy compounds but the chloro compounds gave much poorer yields.

Preparation of *m*-Bromo-aniline.—Nitrobenzene was brominated in the presence of powdered iron as catalyst. The product was fractionally distilled and crystallized from ether; m. p. 52.5°. The *m*-bromonitrobenzene was reduced to *m*-bromo-aniline by the use of concentrated hydrochloric acid and stannous chloride, which gave an 85% yield. The speed of reaction must be controlled by cooling at the beginning, to prevent loss, and after the oil disappeared the mixture was refluxed vigorously for about thirty minutes. The solution was made alkaline, the oil extracted with ether, dried and distilled, giving a light brown product, b. p. 255–259°. Separation by steam distillation was not as satisfactory as extraction with ether.

Preparation of *m*-Bromophenol.—*m*-Bromo-aniline was diazotized and the product hydrolyzed to give *m*-bromophenol. The phenol could not be separated readily by steam distillation, due to formation of resins. The difficulty was overcome by carrying out the hydrolysis of the diazonium salt in an aqueous acid layer, under a benzene layer kept at its boiling temperature. The phenol derivative formed by hydrolysis was dissolved in the benzene layer as rapidly as it formed, and the final product was obtained by distillation of the benzene layer. No resinous by-products were formed and a yield of 76% of the *m*-bromophenol was obtained, b. p. 240–244°. The use of the benzene layer is a modification of a method of general application for prevention of resin formation in such reactions.

Preparation of *m*-Methoxybromobenzene.—The *m*-bromophenol was methylated by the method of Perkin, Ray and Robinson,[5] using dimethyl sulfate on the potassium salt. The mixture was refluxed on the steam-bath for one and a half hours, cooled, extracted with benzene, dried and distilled. The product had a boiling point of 218–221°; yield, 75%.

3,3′-Methoxydiphenyl Oxide.—To 4.1 g. of *m*-methoxyphenol[5] in an evaporating dish was added 1.9 g. of granulated potassium hydroxide, and the mixture heated to 90° until all solid potassium hydroxide had reacted. The temperature was then raised to 200° and the compound stirred for several minutes until the water formed during the reaction was driven off. There was a slight charring during this process. The dried potassium salt was then placed in a small flask with 6.2 g. of *m*-methoxybromobenzene and 0.1 g. of freshly reduced finely divided copper. This mixture was refluxed for six to seven hours at 300–320°; the temperature slowly rose as the reaction proceeded. The mixture was cooled, extracted several times with ether and the ethereal solution washed until the wash water showed very little color. The ether layer was dried over

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[5] Perkin, Ray and Robinson, *J. Chem. Soc.*, 945 (1926).

anhydrous sodium sulfate and fractionated, yield, 26%, giving a viscous oil of low surface tension, with a light brown color and a pleasant odor resembling that of diphenyl oxide; boiling point 332–334°; very soluble in benzene, ether or carbon tetrachloride; slightly soluble in alcohol or ligroin. It is not affected by aqueous potassium hydroxide solution and does not give a color reaction with ferric chloride in dilute alcohol.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.09. Found: C, 73.07, 72.91; H, 5.97, 5.98.

3,3′-Ethoxydiphenyl Oxide.—*m*-Bromophenol was treated with ethyl sulfate and the mixture heated for five hours on the steam-bath; the yield of the *m*-ethoxybromobenzene was 85%; boiling point 228–231°. *m*-Ethoxyphenol was prepared by semiethylation of resorcinol; yield about 43%; boiling point 254–258°. The two monoethoxy compounds were condensed by treatment of the *m*-ethoxyphenol with solid potassium hydroxide and refluxing with *m*-ethoxybromobenzene in the presence of copper catalyst, as in the preparation of the dimethoxyphenyl oxide. The refluxing was continued for ten hours, the temperature slowly climbing to 350°. The ethereal extract when dried and fractionated gave a 36% yield of a pale brown liquid boiling at 341–344°; very soluble in benzene, ether, ligroin or carbon tetrachloride; only slightly soluble in cold alcohol. It is not affected by aqueous potassium hydroxide and does not give a color test with ferric chloride.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.42; H, 6.98. Found: C, 74.22, 74.28; H, 6.93, 7.04.

3-Methoxy-3′-ethoxydiphenyl Oxide.—This compound was prepared by treating *m*-methoxyphenol with solid potassium hydroxide and refluxing with *m*-methoxybromobenzene for eight hours in presence of the copper catalyst. Upon extraction and purification, a 20% yield was obtained, b. p. 338–341°. The compound has a light brown color and a pleasant odor. It is readily soluble in ligroin, benzene, ether or carbon tetrachloride and moderately soluble in cold alcohol. It does not react with potassium hydroxide solution and gives no color reaction with ferric chloride.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.77; H, 6.56. Found: C, 73.59, 73.66; H, 6.71, 6.52.

3,4′-Methoxydiphenyl Oxide.—*p*-Bromophenol was methylated, giving a 75% yield of the *p*-methoxybromobenzene, which was condensed with the potassium salt of *m*-methoxyphenol by refluxing for ten hours in the presence of the copper catalyst. The compound was separated by ether extraction and gave a yield of 30%; b. p. 336–338°. It is a light brown oil with a more pronounced odor than that of the 3-3′-alkoxy derivatives described above. It is less viscous but more soluble in alcohol than the 3,3′-methoxydiphenyl oxide. It is not affected by aqueous potassium hydroxide and gives no color reaction with ferric chloride. In order to determine whether the high temperature of the reaction had caused a rearrangement in position of groups the process was repeated as outlined above, except that the temperature of the reaction was never allowed to rise above 200°, as in the procedure of Ullmann.[6] The time of reaction was increased to thirty-five hours. There was no difference in boiling point between this compound and that formed at the higher temperature.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.09. Found: C, 72.97, 73.17; H, 6.16, 6.05.

2,3′-Methoxydiphenyl Oxide.—*o*-Bromophenol was methylated by treatment with potassium hydroxide and dimethyl sulfate to form *o*-methoxybromobenzene; a yield of 45% was obtained. The latter compound was condensed with *m*-methoxyphenol by

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[6] Ullmann, *Ber.*, **38**, 2211 (1905).

treatment with potassium hydroxide and refluxing at 350° for ten hours in the presence of copper as catalyst. A yield of 33% was obtained, distilling at 326–329°. It has a pleasant odor, crystallizes in small cubical crystals which melt at 33–34° and is soluble in most solvents, though only slightly soluble in ligroin, It is not affected by potassium hydroxide in aqueous solution and gives no color reaction with ferric chloride.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.04; H, 6.09. Found: C, 72.82, 73.18; H, 6.14, 6.02.

Summary

1. Five new alkoxy derivatives of diphenyl oxide were prepared. They are compounds of great stability to alkalies or acids and to heat, of pleasant odor and of low surface tension.

2. In the preparation of phenols for condensation, a new method of procedure was discovered, namely, the hydrolysis of diazonium salts in hot acid solution under a layer of inert solvent, which prevents the formation of tarry by-products by removing the phenol from the acid hydrolyzing solution as rapidly as it is formed.

3. Of several catalysts used, finely divided freshly reduced copper gave the best yields.

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OMEGA-HYDROXY ALIPHATIC ACIDS. II. CONVERSION OF OMEGA-HYDROXYDECANOIC ACID TO CHAIN POLY-INTERMOLECULAR ESTERS AND TO A DIMERIC CYCLIC ESTER[1]

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In a previous paper a satisfactory method of preparation for many ω-hydroxy aliphatic acids was described. Attention was called to the fact that by the action of heat on such acids compounds were produced which appeared to be of high molecular weight. In this investigation these latter compounds are described in more detail. Several other reactions of ω-hydroxy acids have been studied.

A recent paper by W. H. Carothers[3] has given a very clear exposition on polymerization: a proper definition, conditions of ring formation and an introduction to the theory of condensation polymers. The terminology in that publication has been adopted here. As pointed out in a general discussion by Carothers, bi-functional reactions may be either intramolecular or intermolecular. In the first case, the products will be monomeric

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[1] Lycan and Adams, THIS JOURNAL, **51,** 625 (1929).

[2] This paper is an abstract of a thesis submitted by W. H. Lycan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Carothers, THIS JOURNAL, **51,** 2548 (1929).