Summary

1. The use of alkyl sulfates as alkylating agents in typical Friedel-Crafts syntheses has been extended to biphenyl.

2. The general conditions affecting the yield such as reaction time, temperature and proportions of reagents have been studied with the purpose of obtaining a high yield of methylated and ethylated biphenyls.

3. The mono alkyl biphenyls obtained consisted of a mixture of meta and para isomers with the meta isomer predominating. The dialkyl biphenyls also consisted of a mixture of isomers.

4. The structures of the alkylated biphenyls were deduced from analysis and the oxidation to the corresponding acids and their identification.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

The Condensation of Urea with Resorcinol

BY JOHN J. ROEMER[1] AND WILLIAM M. DEGNAN

In an investigation of the possibility of preparing resins from urea and resorcinol, they were heated together for two hours at 125–130° in the presence of anhydrous zinc chloride. A crystalline product melting at 228–229° was isolated from the reaction mixture, and its identification and the assignment of a mechanism to its formation undertaken.

Birnbaum and Lurie[2] caused urea and resorcinol to interact and obtained a product $C_{30}H_{20}N_6O_3$, to which they did not assign a detailed structure. Under our less drastic conditions a product having the molecular formula $C_7H_7NO_3$ was isolated.

This molecular formula indicates the condensation to involve the loss of one mole of ammonia

$$C_6H_6O_2 + CH_4N_2O \longrightarrow C_7H_7NO_3 + NH_3$$

It seemed probable that urea decomposed into cyanic acid and ammonia, and that the former then underwent condensation with resorcinol. Such a condensation might lead to β- or γ-resorcylamide, to *m*-hydroxyphenyl carbamate, or to β-resorcylaldoxime. The last has been reported by Scholl and Bertsch[3] and is not identical with our product.

Condensations of cyanic acid and related compounds with both the ring and the hydroxyl groups of phenols have been reported. The formation of thiobenzamides from isothiocyanates and phenols in the presence of zinc chloride and hydrogen chloride, reported by Karrer,[4] suggests a nuclear condensation, while the formation of *m*-hydroxyphenyl allophanate from pure cyanic acid and resorcinol, in ether solution, reported by Traube[5] suggests involvement of the hydroxyl group, leading to *m*-hydroxyphenyl carbamate.

It was hoped that hydrolysis might lead to one of the known resorcylic acids, thus definitely establishing the nature of our product. However, acid hydrolysis resulted in the loss of carbon dioxide and the formation of resorcinol. The possibility of the displacement of a carboxyl group was recognized and the resorcylamides not eliminated from consideration on this account.

Quantitative bromination should differentiate between *m*-hydroxyphenyl carbamate, which has three positions open for bromination, and β- and γ-resorcylamide, which have only two. Accordingly bromination was carried out in glacial acetic acid to eliminate the possibility of displacement of labile groups, and a dibrominated product was obtained. It was concluded that our product was β- or γ-resorcylamide. In view of the course ordinarily followed by condensations involving resorcinol, the former seemed much more probable.

β-Resorcylamide has been reported by Shoesmith and Haldane[6] as arising from the partial hydrolysis of 2,4-diacetoxy-benzonitrile. Their product melted at 221–222° and corresponded in general with ours. A small sample of material prepared by their method melted at 227–228° and gave no depression of melting point when mixed

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[1] This paper is constructed from a dissertation presented by John J. Roemer to the Faculty of the Graduate School of Indiana University in June, 1940, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Original manuscript received April 20, 1940.

[2] K. Birnbaum and C. Lurie, *Ber.*, **13**, 1619 (1880).

[3] R. Scholl and E. Bertsch, *ibid.*, **34**, 1443 (1901).

[4] P. Karrer and E. Weill, *Helv. Chim. Acta*, **12**, 554 (1921).

[5] W. Traube, *Ber.*, **22**, 1579 (1889).

[6] J. Shoesmith and J. Haldane, *J. Chem. Soc.*, **125**, 113 (1924).

with our product. The structure was further confirmed by acetylation, which gave rise to acetamide and 2,4-diacetylresorcylic acid, identified by comparison with a sample prepared independently. Accordingly we have assigned the structure of β-resorcylamide to our product.

It was possible that cyanamide rather than cyanic acid might have been an intermediate in the condensation reported in this paper and to clarify this point pure cyanamide was substituted for urea in the condensation. No amide was obtained. On the other hand, when potassium cyanate was substituted for urea a yield of 27% of β-resorcylamide was obtained, giving support to our first hypothesis.

Investigation indicates that the condensation, under the conditions employed, is not a general method for the preparation of benzamides. Phenol, catechol, hydroquinone, and phloroglucinol were substituted for resorcinol without leading to amides. Phenylurea, phenyl isocyanate, cyanuric acid and thiourea did not give rise to amides when substituted for urea. Methylurea, nitrourea, and urethan gave 28.4, 22.3 and 0.5%, respectively, of β-resorcylamide.

Experimental

Condensation of Urea with Resorcinol.—A mixture of 7.5 g. of urea, 15 g. of resorcinol, and 25 g. of finely powdered anhydrous zinc chloride was heated to 132° in a 150-cc. flask fitted with a sealed stirrer and a calcium chloride drying tube. The urea and resorcinol formed a light green melt which became more viscous as the reaction proceeded. Motor-stirring was continued as long as possible. At the end of four hours the mixture was an opaque brown solid. It was then cooled and triturated with 100 cc. of water, producing a thick, yellowish, slightly basic suspension. Fifteen cc. of 6 *N* hydrochloric acid was added and the suspension cooled and filtered. The residue was washed with 125 cc. of slightly acidified water. It weighed 10.1 g.

Five grams of the residue was extracted with 125 cc. of boiling water in several portions, leaving an insoluble residue of 0.75 g. The hot water extract was cooled and β-resorcylamide crystallized out. The crude product was dissolved in hot alcohol, decolorized with charcoal, and concentrated to incipient crystallization. Addition of water precipitated the amide. A final recrystallization from hot water gave 3.25 g. (a yield of 34.0%) of long white needles, m. p. 228–229°. The yield can be increased to 40.8% by doubling the proportion of zinc chloride.

Anal. Calcd. for $C_7H_7NO_3$: C, 54.87; H, 4.60; N, 9.15; mol. wt., 153.07. Found: C, 54.78; H, 4.62; N, 9.15; mol. wt. (Rast method), 152.9.

β-Resorcylamide is soluble in ethyl alcohol, acetone, ethyl acetate, hot water, and 1% sodium hydroxide solution. It is moderately soluble in glacial acetic acid, slightly soluble in ether, benzene, carbon disulfide, and chloroform.

Hydrolysis.—Two and one-half grams of β-resorcylamide was refluxed with 50 cc. of 50% sulfuric acid for one-half hour. Carbon dioxide was evolved freely. At the conclusion of the heating period 10 cc. of the dark red solution was made basic and a strong evolution of ammonia noted. The remainder of the acid solution was extracted with ether. The ether was evaporated and resorcinol isolated from the residue and identified as styphnic acid. No β-resorcylic acid could be detected. The use of dilute hydrochloric acid (sp. gr. 1.09) gave similar results.

Bromination.—One gram of β-resorcylamide was dissolved in 35 cc. of glacial acetic acid held at 100°. The delivery end of a buret and a calcium chloride drying tube passed through a rubber stopper in the neck of the reaction flask. A solution of 5 g. of bromine in 50 cc. of glacial acetic acid was added from the buret over a period of one hour. The solution was allowed to stand overnight and the acetic acid was then removed under vacuum at 45–50°. The crystalline residue was dissolved in alcohol, decolorized, and diluted with water. Light cream-colored crystals, m. p. 241–242°, were obtained. The material gave strong qualitative tests for bromine and nitrogen. The molecular weight by the Rast method was 302, which is in satisfactory agreement with that calculated for a dibromo-β-resorcylamide (310.9).

Acetylation.—Five grams of carefully dried β-resorcylamide was dissolved in 25 g. of acetic anhydride in a small flask fitted with a reflux condenser carrying a calcium chloride drying tube. One-half gram of anhydrous zinc chloride was added and the mixture heated at 100° for three hours. The characteristic odor of acetamide was strongly evident. After heating, the reaction mixture was poured into 100 g. of crushed ice. The resultant oil solidified on standing and was purified by dissolving it in saturated potassium bicarbonate solution and acidifying the filtered solution with concentrated hydrochloric acid. The dry product melted at 136–138° and showed no melting point depression when mixed with a sample of diacetyl-β-resorcylic acid prepared by the method of Bergmann and Dangschat.[7]

Potassium Cyanate and Resorcinol.—The apparatus was the same as that for the urea–resorcinol experiment. A mixture of 10.14 g. of potassium cyanate, 15 g. of resorcinol, and 25 g. of anhydrous zinc chloride was heated at 128–132° for four hours, at the end of which the reaction mixture was a hard brown mass. The product was treated in the manner described for the urea–resorcinol experiment and gave 5.1 g. (26.6%) of β-resorcylamide, m. p. 228–229°.

Nitrourea and Resorcinol.—The apparatus used consisted of a three-necked, round-bottomed, 500-cc. flask fitted with a thermometer, a sealed stirrer, a calcium chloride drying tube, and a short length of 20-mm. rubber tubing connected to a 125-cc. Erlenmeyer flask to permit the controlled addition of nitrourea. Thirty grams of resorcinol and 25 g. of anhydrous zinc chloride were placed in the reaction flask and heated to 120°. Thirteen and one-tenth grams of nitrourea was added in very small portions over a period of ninety minutes. Each addition caused effervescence and a small rise in temperature.

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(7) M. Bergmann and P. Dangschat, *Ber.*, **52** 379 (1919).

Heating was continued for two and one-half hours. Treatment of the viscous dark-brown product in the manner described above gave 4.25 g. (a yield of 22.5%) of β-resorcylamide, m. p. 228–229°.

Methylurea and Resorcinol.—The apparatus used was that described for the urea-resorcinol experiment. A mixture of 9.3 g. of methylurea, 15 g. of resorcinol, and 25 g. of anhydrous zinc chloride was heated at 128–132° for four hours, and the residue treated in the manner described above. A crystalline product weighing 5.44 g. was isolated. This melted at 228–229° and was identified as β-resorcylamide, the methyl group being apparently lost as methylamine during the condensation. The yield was 28.4%.

Phenyl Isocyanate and Resorcinol.—When 14.9 g. of phenyl isocyanate, 15 g. of resorcinol, and 25 g. of zinc chloride were heated at 128–132° for four hours, and the residue treated in the usual manner, a large crop of white crystals identified as the diphenyl-diurethan of resorcinol, m. p. 164°, was isolated. No other identifiable product was obtained.

Urethan and Resorcinol.—A mixture of 11.1 g. of urethan, 15 g. of resorcinol, and 25 g. of anhydrous zinc chloride was heated at 128–132° for four hours. The viscous clear red residue was treated in the usual manner, yielding 0.1 g. of β-resorcylamide, a yield of only 0.5% of the theoretical. A large amount of unreacted resorcinol was recovered from the mother liquors.

Summary and Conclusions

1. When resorcinol and urea are allowed to react at 128–132° in the presence of anhydrous zinc chloride, β-resorcylamide is formed.
2. The evidence indicates that cyanic acid is an intermediate in this reaction.
3. Under the conditions employed the reaction is not general for the synthesis of benzamides.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF PENNSYLVANIA]

α-Chloro-α-sulfonylamides

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In continuing[2] the study of sulfones containing "positive halogen," α-chloro-α-sulfonylamides were selected to serve as examples of the activation of chlorine by sulfone groups in the alpha position. The chlorination of α-sulfonylamides in glacial acetic acid gave satisfactory yields of the desired products. Their structures seem established (1) by analogy with the corresponding products from bromination,[2] (2) by the increased difficulty of chlorination of the butyramides[2] and (3) by the preparation of I by an alternative method which leaves no doubt that chlorine is attached to carbon.

$$\mathrm{RSO_2CHR'CONH_2} \xrightarrow{\mathrm{Cl_2}} \mathrm{RSO_2CClR'CONH_2}$$

	R =	R' =
I	p-$CH_3C_6H_4$—	H—
II	p-$CH_3C_6H_4$—	Cl—
III	p-$CH_3C_6H_4$—	C_2H_5—
IV	n-C_4H_9—	Cl—
V	n-C_4H_9—	CH_3—
VI	n-C_4H_9—	C_2H_5—

The α-chloro-α-sulfonylamides were considerably more reactive than the corresponding α-bromo-α-sulfonylamides.[2] The former were in some cases dehalogenated by attempted recrystallization from dilute alcohol or water. One α,α-dichloro derivative (II) was converted to the monochloro product (I) by repeated recrystallization from alcohol containing water and repeated recrystallization of I from water gave α-p-tolylsulfonylacetamide. α-Chloro-α-p-tolylsulfonyl-n-butyramide (III) and II were decomposed by moisture in the atmosphere and could not be stored except under anhydrous conditions. Aside from this increased reactivity, the chloro compounds behaved like the bromo derivatives and reacted with hydrazine, hydriodic acid, piperidine and mercaptides to give nitrogen, iodine, piperidine hydrochloride and disulfides, respectively.

The less successful methods tested for the preparation of α-chloro-α-sulfonylamides are worthy of brief mention. The reaction of dichloroacetamide with sodium p-toluenesulfinate gave α-chloro-α-p-tolylsulfonylacetamide (I), but the yield was small and the product difficult to purify. While this is unsatisfactory as a preparative method, this experiment offers verification of the structure of the products obtained by direct chlorination.

The reaction of mercaptides with dichloroacet-

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(1) Röhm and Haas Research Assistant.

(2) For previous work see Ziegler and Connor, THIS JOURNAL, **62**, 1049 (1940); *ibid.*, **62**, 2596 (1940).