Summary

The preparation of a series of disubstituted phenyldichloroarsines and phenylarsine oxides is described.

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Alkylation of Biphenyl Using Alkyl Sulfates in Friedel–Crafts Syntheses

BY JACK EPELBERG AND ALEXANDER LOWY

The purpose of this investigation has been to extend the use of dimethyl sulfate and diethyl sulfate as alkylating agents in typical Friedel–Crafts syntheses to biphenyl. Alkyl sulfates have distinct advantages as alkylating agents over the lower alkyl halides and olefins in that they eliminate the necessity for pressure apparatus or very high stirring speeds. The higher boiling points of the alkyl sulfates are also advantageous in that they permit a higher reaction temperature.

The Friedel–Crafts reaction needs no discussion here since it is covered admirably by several comprehensive reviews.[2–5]

Kane and Lowy[6] have shown that satisfactory yields of monoalkylated benzenes can be obtained by condensing dimethyl, diethyl, diisopropyl and dibutyl sulfate with benzene in the presence of aluminum chloride.

With biphenyl the reaction may be summarized by the equation

$$3(RO)_2SO_2 + 6C_{12}H_{10} + 2AlCl_3 \longrightarrow 6C_{12}H_9R + 6HCl + Al_2(SO_4)_3$$

It was desirable to determine the position of the entering alkyl groups and in order to accomplish this, an oxidation of each alkylated product was carried out and a study of the oxidation products made. The oxidation products isolated indicated that the monoalkylated products consisted of a mixture of meta and para isomers with the meta predominating. The dialkylated products consisted of a mixture of various isomeric dialkyl biphenyls.

Experimental

The apparatus employed for the alkylations was the usual one-liter three-necked flask, into one neck of which extended a dropping funnel and thermometer. The central neck was fitted with a mercury seal and a motor-driven glass stirrer. The third neck was connected to a modified Hopkins-type reflux condenser. This condenser could be cooled by water, or it could be packed with solid carbon dioxide. This latter procedure was employed when dimethyl sulfate was the reactant. Fractionations were conducted with a twelve-plate column packed with helices.[7,8] By means of a constant pressure regulator the pressure could be maintained constant throughout the fractionation. A reflux ratio of 1:12 to 1:15 was used.

The aluminum chloride used throughout was of 99.5% purity. The biphenyl was recrystallized from hot alcohol (m. p. 70°). The alkyl sulfates were purified by vacuum distillation before use.

Diethyl Sulfate.—A large series of experiments was conducted in which the general conditions affecting the yield such as reaction time, temperature, solvent, rate of addition and proportions of reagents have been studied. With diethyl sulfate as the alkylating agent these experiments showed that low temperatures and longer reaction time favored high yields. The best yield resulted with a ratio of diethyl sulfate to biphenyl to aluminum chloride of $1^1/_2:1:1^1/_8$. This experiment is described here.

Biphenyl (308 g., 2 moles) was stirred with *o*-dichlorobenzene (680 cc.). When the biphenyl had gone into solution, aluminum chloride (300 g., 2.25 moles) was added. The reaction mixture was cooled on an ice-bath (5–8°). Diethyl sulfate (462 g., 3 moles) was then added dropwise during four and one-half hours. At the end of ten hours the ice-bath was removed and the reaction allowed to proceed at 24° for a period of four hours, making a total reaction time of fourteen hours. Throughout this time there was a rapid evolution of hydrogen chloride. The reaction product was poured over cracked ice acidified with 200 cc. of hydrochloric acid and allowed to hydrolyze overnight. The top oily layer was decanted, the remainder extracted with benzene. The benzene was distilled and the remaining oil combined with the first portion. The oil was first washed with aqueous sodium carbonate, water and then dried over anhydrous calcium chloride. The *o*-dichlorobenzene was first removed by vacuum distillation, and the distillation continued until the excess unreacted biphenyl

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[1] Abstracted from a thesis presented by Jack Epelberg to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree. Presented at the Detroit meeting of the A. C. S. Sept., 1940.

[2] G. Kränzlein, "Aluminiumchlorid in der organischen Chemie," Verlag Chemie G. m. b. H., Berlin, revised edition, 1932.

[3] N. O. Calloway, *Chem. Rev.*, **17**, 327 (1935).

[4] P. H. Groggins, "Unit Processes in Organic Synthesis," McGraw-Hill Book Co., Inc., New York, N. Y., second edition, 1938.

[5] D. V. Nightingale, *Chem. Rev.*, **25**, 329 (1939).

[6] H. L. Kane and A. Lowy, THIS JOURNAL, **58**, 2605 (1936).

[7] F. C. Whitmore and A. R. Lux, *ibid.*, **54**, 3451 (1932).

[8] C. D. Wilson, G. T. Parker and K. C. Laughlin, *ibid.*, **55**, 2795 (1933).

27 g.) was removed. There now remained 363 g. of oil consisting of various ethylated biphenyls. Attempts to fractionate this oil by ordinary methods and columns proved unsuccessful. No sharp fractions could be obtained. However, when a twelve-plate packed column was used, fractionation into the mono-, di- and higher ethylated biphenyls could be obtained: (I) 30 cc. 135–136°; (II) 16 cc. 136–159°; (III) 78 cc. 159–166°; (IV) 15 cc. 166–178°; (V) 123 cc. 178–192°. (III) and (V) were refractionated. (III) the ethylbiphenyl boiled at 160–164° at 20 mm. and (V) the diethylbiphenyl boiled at 181–185° at 20 mm.

Dimethyl Sulfate.—Before a technique was evolved which led to a satisfactory yield of methylated biphenyls a series of experiments was carried out under varying conditions. In general the yields with dimethyl sulfate were not as good as with the diethyl sulfate. It also required larger amounts of alkylating agent as well as increased temperature in the case of the dimethyl sulfate. The best yield was obtained when the ratio of dimethyl sulfate to biphenyl to aluminum chloride was $2^{1}/_{2}$:1:1.44 and the temperature kept at 42°. This experiment is described here.

Biphenyl (308 g., 2 moles) was stirred with *o*-dichlorobenzene (680 cc.). When the biphenyl had gone into solution aluminum chloride (384 g., 2.88 moles) was added. The reaction mixture was placed on a water-bath maintained at 42° throughout the course of reaction. The dimethyl sulfate (630 g., 5 moles) was added dropwise during a period of four and one-half hours. The reaction was allowed to proceed for five and one-half hours longer, making a total reaction time of ten hours. During the entire experiment the reflux condenser was packed with solid carbon dioxide. At the end of the stated time the reaction product was poured over cracked ice acidified with 280 cc. of hydrochloric acid and allowed to hydrolyze overnight. The top oily layer was decanted and extracted with benzene. The bottom layer was likewise extracted. The two benzene layers were combined and washed with aqueous sodium carbonate and water and then dried over anhydrous calcium chloride. The dried oil was then distilled to remove the benzene, *o*-dichlorobenzene and unreacted biphenyl. The remaining 268 g. of oil was then fractionated with the packed column referred to previously: (1) 60 cc. 135–137°; (II) 22 cc. 137–149°; (III) 80 cc. 149–152°; (IV) 18 cc. 152–163°; (V) 68 cc. 163–170°; (VI) 17 cc. 170–181°; (VII) 23 cc. 181–185°. (III) and (V) were refractionated. (III) the methylbiphenyl boiled at 149–151° at 20 mm. and (V) the dimethylbiphenyl boiled at 163–167° at 20 mm.

Proof of Structure of Alkylated Biphenyls.—Molecular weight determinations on the apparatus devised by Hanson and Bowman[9] gave the following results. For biphenyl, calcd., 154; found, 159.4, 159.4, 157.6, 157.6; for ethylbiphenyl, calcd. 182; found, 185.4, 184.5, 186.1; and for diethylbiphenyl, calcd. 210; found, 213.5, 214.2, 214.2.

The structure of the alkylated biphenyls was further substantiated by carbon and hydrogen analysis.

Anal. Methylbiphenyl. Calcd. for $C_{13}H_{12}$: C, 92.74; H, 7.26. Found: C, 92.99, 92.49; H, 7.46, 7.18.

Anal. Dimethylbiphenyl. Calcd. for $C_{14}H_{14}$: C, 92.31; H, 7.69. Found: C, 92.58, 92.64; H, 7.63, 7.77.

Anal. Ethylbiphenyl. Calcd. for $C_{14}H_{14}$: C, 92.31; H, 7.69. Found: C, 92.09, 92.11, 92.24; H, 7.73, 7.49, 7.92.

Anal. Diethylbiphenyl. Calcd. for $C_{16}H_{18}$: C, 91.43; H, 8.51. Found: C, 91.47, 91.15; H, 8.47, 8.49.

Oxidation.—When methylbiphenyl was oxidized with chromic acid and sulfuric acid (1:3 water), there was formed a mixture of terephthalic acid and benzoic acid. The terephthalic acid was identified by converting it to the dimethyl ester which melts at 141°, also by determining its neutralization equivalent (88). The benzoic acid (m. p. 121°) was converted to benzanilide (m. p. 160°). When the oxidations were conducted with a milder oxidizing agent such as potassium permanganate solution (2%), there was formed a mixture of *m*-phenylbenzoic acid (m. p. 161°) and *p*-phenylbenzoic acid (m. p. 224°). These acids were separated by means of their difference in solubility in 10% sodium carbonate solution. The *p*-phenylbenzoic acid is only slightly soluble in sodium carbonate solution. Since much more *m*-phenylbenzoic than *p*-phenylbenzoic acid was obtained in all experiments, it would seem to indicate that the meta isomer predominates in the meta–para mixture. These acids were identified by their neutralization equivalents (196.5, 198), by further oxidation with chromic acid to isophthalic and terephthalic acids, by heating with calcium oxide and identifying the biphenyl formed and finally by carbon and hydrogen analysis.

Anal. *m*-Phenylbenzoic acid. Calcd. for $C_{13}H_{10}O_2$: C, 78.79; H, 5.05. Found: C, 78.84, 78.70; H, 5.34, 4.93. *p*-Phenylbenzoic acid. Found: C, 78.83, 79.11; H, 5.08, 4.98.

The fact that both meta and para acids were formed indicated that the methylbiphenyl consisted of a mixture of meta and para isomers.

Oxidation of dimethylbiphenyl with chromic and sulfuric (1:3 water) likewise gave terephthalic and benzoic acids. These were identified as above. When oxidized with 2% permanganate, there resulted a mixture of dibasic acids. Although these acids could not be separated, their presence was shown by neutralization equivalents, carbon and hydrogen analysis and conversion to corresponding esters. The neutralization equivalents obtained were 122.6, 117.6. Proof of the presence of the following acids was obtained by separation of the dimethyl esters.

Acid	Ester m. p., °C.
4,4′-Biphenyldicarboxylic acid	212
3,4′-Biphenyldicarboxylic acid	98.5
2,3′-Biphenyldicarboxylic acid	69

These esters were separated by means of their difference in solubility in alcohol.

Anal. Biphenyldicarboxylic acid. Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.13. Found: C, 69.28, 69.64; H, 4.30, 4.29.

Oxidation of ethylbiphenyl gave results analogous to methylbiphenyl. Chromic acid and sulfuric acid (1:3 water) gave terephthalic and benzoic acids. Oxidation with permanganate gave *m*-phenylbenzoic acid. Diethylbiphenyl also gave analogous results on oxidation with both chromic acid and permanganate solution. These acids were identified as were those described above.

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(9) W. E. Hanson and J. R. Bowman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 440 (1939).

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

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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).