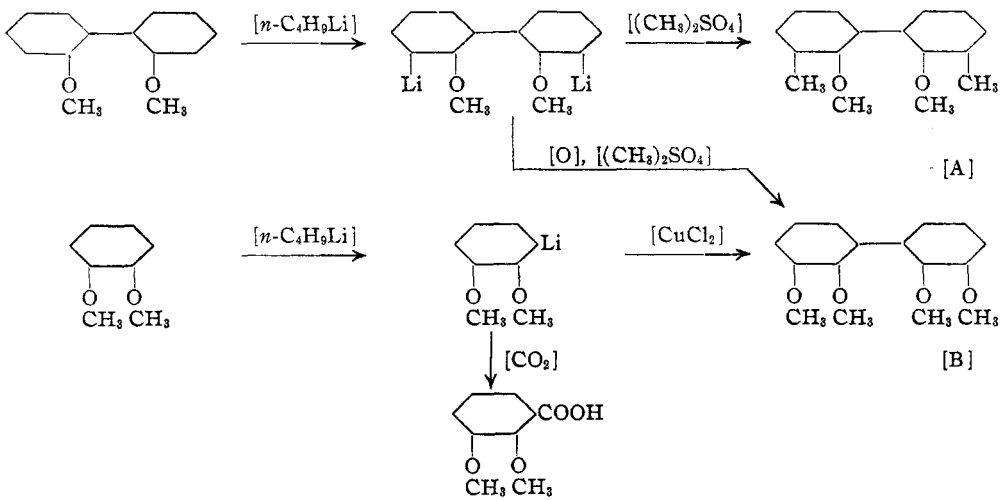
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. XIX. Derivatives of 2,2'-Dihydroxybiphenyl*

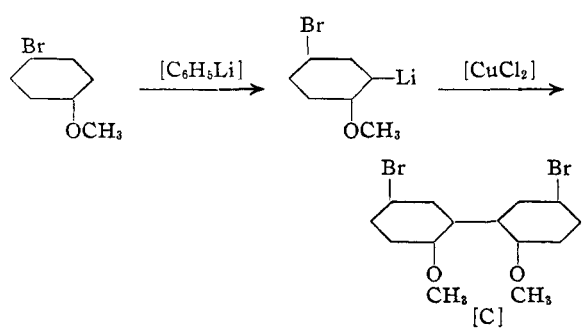
BY HENRY GILMAN, JACK SWISS AND LEE C. CHENEY

Incidental to studies on the preparation of difficultly accessible dibenzofuran derivatives from derivatives of 2,2'-dihydroxybiphenyl by ring closure reactions, some new biphenyl compounds have been prepared and their structures determined. In addition, the structures of some previously reported[1] bromine substitution products of 2,2'-dihydroxybiphenyl have been established.



2,2'-Dimethoxybiphenyl is dimetalated by *n*-butyllithium in good yields, the lithium atoms entering the positions ortho to the ether linkages, in accordance with earlier general observations.[2] That the metal atoms were in the 3,3'-positions was shown by two different procedures. First, the dilithium compound was treated with methyl sulfate to give 3,3'-dimethyl-2,2'-dimethoxybiphenyl [A] which was then compared with an authentic specimen.[3a] Second, veratrole was metalated by *n*-butyllithium and the position of the lithium atom was determined by carbonation which gave veratrole-3-carboxylic acid, characterized as its methyl ester. 3-Veratryllithium was then treated with anhydrous cupric chloride in ether and the 2,2',3,3'-tetramethoxybiphenyl [B] resulting from the coupling, was found to be identical with the tetramethoxy compound formed by oxidation of the dimetalation product of 2,2'-dimethoxybiphenyl and subsequent methylation.

The x,x'-dibromo-2,2'-dihydroxybiphenyl of Diels and Bibergeil[1] was shown to be 5,5'-dibromo-2,2'-dihydroxybiphenyl by methylation and comparison of the dimethoxy compound with authentic 5,5'-dibromo-2,2'-dimethoxybiphenyl [C] synthesized from 5-bromo-2-methoxyphenyllithium and cupric chloride in ether.



This structure was also established by halogen–metal interconversion of the dibromo-2,2'-dimethoxybiphenyl with *n*-butyllithium, followed by carbonation, which gave 2,2'-dimethoxy-5,5'-biphenyldicarboxylic acid,[3b] characterized as its dimethyl ester.[3b]

Two of the bromine atoms in the x,x,x',x'-tetrabromo-2,2'-dihydroxybiphenyl of Diels and Bibergeil[1] were shown to be in the 5,5'-positions

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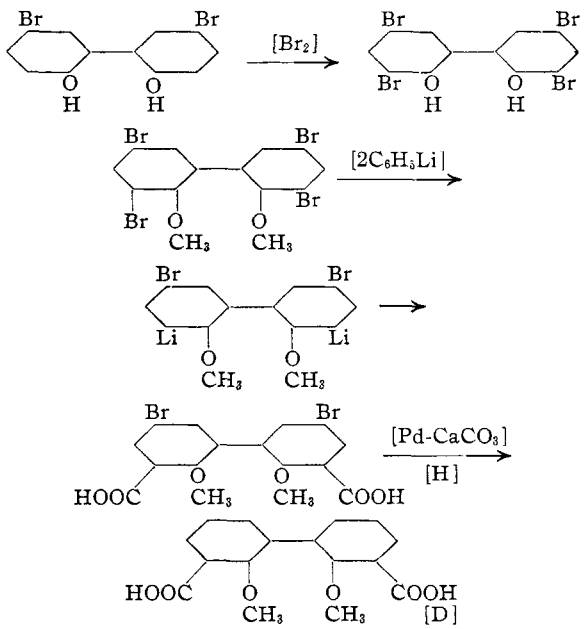
(1) Diels and Bibergeil, *Ber.*, **35**, 302 (1902).

(2) See, Gilman, Cheney and Willis, THIS JOURNAL, **61**, 951 (1939), for leading references.

(3) (a) Sugii and Shindo, *J. Pharm. Soc. Japan*, **54**, 829 (1934). Professor Sugii kindly provided the sample for the mixed melting point determination. (b) Sugii, *ibid.*, **50**, 183 (1930) [*C. A.*, **24**, 3505 (1930)].

by the formation of their compound upon further bromination of 5,5′-dibromo-2,2′-dihydroxybiphenyl. The positions of the remaining two bromines were determined by methylation of the tetrabromo compound, treatment of the dimethoxy compound with two equivalents of phenyllithium, carbonation and dehalogenation to give 2,2′-dimethoxy-3,3′-biphenyldicarboxylic acid [D]



The independence of the two benzenoid nuclei in 2,2′-dimethoxybiphenyl is strikingly illustrated by the ease with which this compound undergoes dimetalation with *n*-butyllithium. Dibenzofuran, which contains a single ether linkage, cannot be dimetalated by *n*-butyllithium under customary conditions. An interesting case of dimetalation of thiophthen by ethylmagnesium bromide under drastic conditions has just been reported.[4]

Experimental Part

2,2′-Dihydroxybiphenyl.—This compound was readily prepared from dibenzofuran according to directions supplied by Dr. Edgar C. Britton.[5] An iron bomb tube, containing an intimate mixture of 100 g. (0.6 mole) of technical dibenzofuran, 50 g. of flake sodium hydroxide and 50 g. of potassium hydroxide was heated in a Carius furnace at 400–410° for eight hours. The solid was removed from the bomb with steam and hot water, the excess alkali was nearly neutralized with sulfuric acid and then Norit was added and the solution was filtered. From the filtrate there was obtained by acidification with sulfuric acid 38.6 g. (28.6%) of crude pale gray 2,2′-dihydroxybiphenyl monohydrate. Purification with slight loss was accomplished by dissolving the hydrate in toluene (16 g. per 100 cc. of solvent), distilling until no more water came over, filtering and cooling. The anhydrous white crystals thus obtained melted at 108–109°.

2,2′-Dimethoxybiphenyl.—The procedure of Borsche and Scholten[6] was used. To a stirred solution of 123 g. (0.603 mole) of crude 2,2′-dihydroxybiphenyl monohydrate in 635 cc. of 10% sodium hydroxide solution was added dropwise 178 g. (1.41 moles) of methyl sulfate. After three and one-half hours the mixture was chilled and the white granular product was separated by filtration and was washed and dried. The yield of crude material (m. p. 148.5–152.5°) was 112.2 g. or 87%. Recrystallization from benzene or from a large volume of alcohol produced colorless crystals, m. p. 154–155°.

3,3′-Dimethyl-2,2′-dimethoxybiphenyl (A).—To 21.5 g. (0.10 mole) of 2,2′-dimethoxybiphenyl dissolved in 150 cc. of ether was added a solution of *n*-butyllithium prepared from 8.5 g. (1.20 g. atoms) of lithium, 63 cc. (0.60 mole) of *n*-butyl bromide, and 200 cc. of ether. The resultant mixture was stirred for twenty-four hours at the reflux temperature and then allowed to stand for an additional eight hours at room temperature. To this mixture was added dropwise 50 g. (0.40 mole) of methyl sulfate dissolved in 100 cc. of ether. The addition of the methyl sulfate caused vigorous refluxing. The excess methyl sulfate was destroyed by sodium hydroxide and the brownish oil obtained subsequent to removal of the solvent was distilled (b. p. 152° (8 mm.)). The pale yellow oil which distilled over weighed 11.0 g. (45%).

This oil was refractionated through an electrically heated column and the colorless fraction boiling at 137.5–138.5° (5 mm.) was collected. This colorless oil which did not crystallize on cooling was taken up in ethanol, from which it crystallized as needles melting at 53–55°. Two recrystallizations from the same solvent raised the melting point to 59–61°. A mixed melting point determination with an authentic specimen of 3,3′-dimethyl-2,2′-dimethoxybiphenyl (m. p. 60–61°)[3a] gave a melting point of 60–61°.

The above experiment establishes the fact that in the dimetalation of 2,2′-dimethoxybiphenyl with *n*-butyllithium the lithium atoms enter the 3,3′-positions. Consequently the diacid obtained by carbonation of the dimetalation product must be 2,2′-dimethoxy-3,3′-biphenyldicarboxylic acid. Likewise the dihydroxy compound obtained by oxidation of the dimetalation product must be 2,2′-dimethoxy-3,3′-dihydroxybiphenyl.

It follows also that the mono-acid and mono-hydroxy compound obtained as by-products in the carbonation and oxidation reactions described in the following sections have their carboxyl and hydroxyl groups, respectively, in the 3-position.

2,2′-Dimethoxy-3,3′-biphenyldicarboxylic Acid (D).—To a suspension of 18.6 g. (0.087 mole) of 2,2′-dimethoxybiphenyl in 60 cc. of ether was added 0.2 mole of *n*-butyllithium in 500 cc. of ether. The mixture was stirred and refluxed for twenty hours and then was carbonated by pouring it upon an excess of crushed solid carbon dioxide.

(4) Challenger and Gibson, *J. Chem. Soc.*, 305 (1940).

(5) E. W. Smith, Doctoral Dissertation, Iowa State College (1936), p. 98. The authors are grateful to Dr. Britton and to Dr. Smith for assistance. See, particularly, Kraemer and Weissberger, *Ber.*, **34**, 1662 (1901).

(6) Borsche and Scholten, *ibid.*, **50**, 607 (1917).

The resulting mixture was extracted twice with 5% sodium hydroxide solution. During the process about 200 cc. of benzene was added to the separatory funnel to dissolve some alkali-insoluble material. From the alkaline extracts there was obtained 22.2 g. of amorphous acid, the major portion melting at 193–196°. Recrystallization from acetic acid gave 13.1 g. (49.9%) of 2,2'-dimethoxy-3,3'-biphenyldicarboxylic acid melting at 205–206°. Further recrystallization from the same solvent gave a final melting point of 208–209°.

Anal. Calcd. for $C_{16}H_{14}O_6$: neut. equiv., 151. Found: neut. equiv., 150.

Dilution of the combined acetic acid mother liquors with water caused the precipitation of 6.7 g. of material (m. p. 163–199°) which was treated with a solution of 1.75 g. of potassium hydroxide in 10 cc. of water. The potassium salt of the dibasic acid which separated was filtered off and the filtrate was diluted to a volume of 125 cc. and acidified. The sticky solid thus obtained was recrystallized twice from dilute alcohol and once from petroleum ether (b. p. 77–115°) to yield 2.1 g. (9.3%) of **2,2'-dimethoxy-3-biphenylcarboxylic acid,** m. p. 114.5°.

Anal. Calcd. for $C_{15}H_{14}O_4$: methoxyl, 24.05. Found: methoxyl, 24.00.

One-tenth gram of the dibasic acid was treated with an excess of diazomethane in ether. The resulting ester was recrystallized from methanol and from petroleum ether (b. p. 60–68°). The colorless granular crystals of **dimethyl 2,2'-dimethoxy-3,3'-biphenyldicarboxylate** melted at 76–77°.

Anal. Calcd. for $C_{18}H_{18}O_6$: methoxyl, 37.60. Found: methoxyl, 37.65.

A mixture of 2.5 g. (0.0075 mole) of the dibasic acid and 10 cc. of constant boiling hydriodic acid was refluxed vigorously for two hours and then poured into 175 cc. of water. The white solid thus obtained was recrystallized from ethanol to yield 1.76 g. (61%) of **2,2'-dihydroxy-3,3'-biphenyldicarboxylic acid** which melted at 304° with decomposition (some decomposition began to take place at about 280°).

Anal. Calcd. for $C_{14}H_{10}O_6$: C, 61.25; H, 3.69. Found: C, 61.46; H, 3.84.

An alcoholic solution of the hydroxy-acid gave a purple color with ferric chloride solution.

Two attempts to effect a ring closure of the dihydroxy compound to 4,6-dibenzofurandicarboxylic acid were unsuccessful. (I) A mixture of 2 g. of 2,2'-dihydroxy-3,3'-biphenyldicarboxylic acid and 20 cc. of hydrobromic acid (sp. gr. 1.49) was heated in a sealed tube at 240–250° for five hours. There was obtained a nearly quantitative yield of dibenzofuran; complete decarboxylation had attended ring closure. (II) An intimate mixture of 1.5 g. of the dicarboxylic acid and 7.5 g. of anhydrous zinc chloride was heated in a sealed tube for five hours at 240–250°. Again dibenzofuran was obtained in nearly quantitative yield. Greater success may attend the cyclization of the corresponding di-ester.

2,2' - Dimethoxy - 3 - hydroxybiphenyl.—*n* - Butyllithium, prepared from 110 g. (0.8 mole) of *n*-butyl bromide, 12.3 g. (1.76 g. atoms) of finely cut lithium and 750 cc. of ether, was strained through glass wool into a suspension of 42.8 g. (0.2 mole) of 2,2'-dimethoxybiphenyl in 400 cc. of ether. The mixture was stirred and refluxed for twenty hours, cooled below 2°, and then 0.4 mole of *n*-butylmagnesium bromide in 200 cc. of ether was added (modified Ivanoff procedure[7]) and dry oxygen was slowly swept over the surface of the cold mixture (the temperature was maintained below 2°) until a negative color test was observed.[8]

After hydrolysis with ice and hydrochloric acid the suspended starting material (7.1 g., 16.5%) was filtered out and the aqueous layer was extracted with ether and then discarded. The ether extracts were added to the ether layer which was then extracted with 5% sodium hydroxide solution until all acidic material had been removed. The alkaline solution was treated with Norit, boiled to remove dissolved ether, filtered, acidified and cooled. The pinkish tan solid thus obtained (25.7 g., m. p. 102–106°) was treated with a hot solution of 8.6 g. of sodium hydroxide in 50 cc. of water, and additional water was slowly added to the heated suspension until all dissolved. Cooling precipitated a lustrous salt which was removed by filtration. Concentration of the filtrate yielded a second crop of the sodium salt. The combined precipitates were dissolved in hot water and the water solution acidified to yield downy needles which melted at 114–115°. Recrystallization from 30% ethanol gave 15.3 g. (33.2%) of needles, m. p. 115–116°. A further recrystallization from petroleum ether (b. p., 60–68°) did not alter the melting point.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.2; H, 6.09; active hydrogen, 1.0. Found: C, 73.2 and 73.4; H, 6.11 and 6.17; active hydrogen (by semi-micro Zerewitinoff analysis), 1.03.

An alcoholic solution of this compound gave a green color with 1% ferric chloride solution.

The dark brown filtrate from the sodium salt of the monohydroxy derivative was warmed, acidified and cooled. The brown solid thus obtained was recrystallized from water to yield 2.45 g. of material, m. p. 156–169°. Three crystallizations from alcohol yielded 0.7 g. (1.42%) of colorless crystals of **2,2'-dimethoxy-3,3'-dihydroxybiphenyl,** m. p. 174.5–175.5°.

Anal. Calcd. for $C_{14}H_{14}O_4$: methoxyl, 25.20. Found: methoxyl, 25.30.

2,2',3,3'-Tetramethoxybiphenyl [B].—One-tenth gram of 2,2'-dimethoxy-3,3'-dihydroxybiphenyl obtained by oxidation of the corresponding dilithium compound was treated with an excess of diazomethane in ether. The reaction was extremely sluggish; only a few bubbles of nitrogen were given off. Following removal of the solvent there was obtained an oil instead of the expected solid. The oil was then treated with alkali and excess methyl sulfate. This gave a solid which melted at 93–97°. A recrystallization from petroleum ether (b. p. 28–38°) and from methanol raised the melting point to 104–105°. A mixed melting point determination with the authentic 2,2',3,3'-tetramethoxybiphenyl prepared by coupling showed no depression.

Metalation of Veratrole.—To 3.45 g. (0.025 mole) of veratrole in 20 cc. of ether was added 0.05 mole of *n*-

(7) Ivanoff, *Bull. soc. chim.*, **39**, 47 (1926).

(8) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

butyllithium in 80 cc. of ether. The solution was stirred at room temperature for twenty-two hours and then carbonated by pouring it upon crushed solid carbon dioxide. The mixture was extracted with several portions of dilute potassium hydroxide solution, which were combined and acidified to yield 2.55 g. (56%) of colorless needles, m. p. 120–122°. An additional 0.4 g. of acid melting at 115–120° was obtained by extraction of the water layer with ether (combined yield, 64.8%). The methyl ester, prepared from the acid and diazomethane, melted at 57° after crystallization from petroleum ether (b. p., 28–38°). The melting points reported for 2,3-dimethoxybenzoic acid[9] and its methyl ester[10] are 122° and 57.5°, respectively.

Cupric Chloride with 3-Veratryllithium.—To 0.05 mole of *n*-butyllithium in 40 cc. of ether was added 5.52 g. (0.04 mole) of veratrole in 40 cc. of ether. After twenty-two hours of stirring at room temperature 13.45 g. (0.1 mole) of anhydrous cupric chloride was added in several portions. There was no evidence of reaction and after one and one-half hours of additional stirring the color test[8] was strongly positive. At this point 50 cc. of benzene was added and the solution was refluxed for four hours, after which time the color test was negative. Subsequent to addition of water and removal of the solvent there was obtained 0.1 g. (1.8%) of product which melted at 98–100°, and 3.5 g. (63.5%) of veratrole was recovered. Recrystallization of the 2,2',3,3'-tetramethoxybiphenyl from methanol gave white needles, m. p. 104–105°.

Anal. Calcd. for $C_{16}H_{18}O_4$: methoxyl, 45.25. Found: methoxyl, 45.00.

This substance showed no depression in melting point when mixed with the 2,2',3,3'-tetramethoxybiphenyl prepared from 2,2'-dimethoxybiphenyl by metalation, oxidation and subsequent methylation.

5,5'-Dibromo-2,2'-dimethoxybiphenyl [C].—To 34.4 g. (0.10 mole) of the x,x'-dibromo-2,2'-dihydroxybiphenyl, prepared in accordance with the directions of Diels and Bibergeil,[1] dissolved in 106 cc. (0.265 mole) of 10% sodium hydroxide solution, was added, dropwise, 22 cc. (29.8 g., 0.235 mole) of methyl sulfate. When all of the methyl sulfate had been added the mixture was refluxed for ninety minutes. Upon cooling there was obtained 34 g. (92%) of white needles, m. p. 125–128°. Recrystallization from ethanol raised the melting point to 129–130°.

Anal. Calcd. for $C_{14}H_{12}O_2Br_2$: Br, 43.00. Found: Br, 43.04 and 43.17.

This compound showed no depression in melting point when mixed with authentic 5,5'-dibromo-2,2'-dimethoxybiphenyl prepared by metalation of *p*-bromoanisole with subsequent coupling of the metalation product.

Cupric Chloride with 5-Bromo-2-methoxyphenyllithium.—To 9.4 g. (0.05 mole) of *p*-bromoanisole in 15 cc. of ether was added 0.04 mole of phenyllithium in 35 cc. of ether. The clear solution was stirred for a few minutes and then allowed to stand at room temperature for twenty hours. Then 10 g. (0.074 mole) of anhydrous cupric chloride was added and the mixture was refluxed for one-half hour. The solution was washed with water, the ether layer separated and dried over calcium chloride and then the ether was distilled off. Upon cooling the residue there was obtained 1.4 g. (18.8%) of brownish white needles which melted at 115–118° after being washed with methanol. A recrystallization from ethanol raised the melting point to 130–131° and further recrystallization did not change the melting point.

A mixed melting point with the dibromo-2,2'-dimethoxybiphenyl (m. p. 129–130°) prepared by bromination of 2,2'-dihydroxybiphenyl followed by methylation showed no depression. Since it has been established[11] that 5-bromo-2-methoxyphenyllithium results from the metalation of *p*-bromoanisole with phenyllithium, it follows that this coupling product is 5,5'-dibromo-2,2'-dimethoxybiphenyl.

5,5'-Dibromo-2,2'-dimethoxybiphenyl with *n*-Butyllithium.—To 3.72 g. (0.01 mole) of 5,5'-dibromo-2,2'-dimethoxybiphenyl in 50 cc. of 1:1 ether–benzene was added 0.05 mole of *n*-butyllithium in 50 cc. of ether. The mixture was stirred at room temperature for forty minutes and then carbonated. There was obtained 1.9 g. (63%) of acid, free of inorganic salts, which melted at 335–340° with decomposition.

One-tenth gram of the acid was decarboxylated by being refluxed for ninety minutes with 2 cc. of isoquinoline and 0.2 g. of copper powder. After removal of the isoquinoline by extraction with hydrochloric acid the residue was washed with alkali and then extracted with hot ethanol, from which were deposited white needles, m. p. 150–153°. Recrystallization from ethanol gave a product which melted at 153–154° and which was identified as 2,2'-dimethoxybiphenyl by the method of mixed melting points.

The methyl ester prepared from the acid and diazomethane melted at 173–174° after recrystallization from methanol. This agrees with the melting point (173–174°) reported by Sugii[3b] for dimethyl 2,2'-dimethoxy-5,5'-biphenyldicarboxylate. The corresponding acid is reported as melting above 300°.[3b]

5,5'-Dibromo-2,2'-diacetoxybiphenyl.—Ten grams (0.029 mole) of 5,5'-dibromo-2,2'-dihydroxybiphenyl was suspended in 25 cc. of acetic anhydride and 5 drops of concd. sulfuric acid was added. The resulting solution was heated for an hour on a steam-bath, then was thoroughly cooled, and finally was poured slowly into 200 cc. of cold water. There was obtained after recrystallization from ethanol 9.7 g. (78%) of the diacetoxy compound which melted at 105–106°.

Anal. Calcd. for $C_{16}H_{12}O_4Br_2$: Br, 37.40. Found: Br, 37.41 and 37.50.

The **mono-*p*-toluenesulfonyl ester of 5,5'-dibromo-2,2'-dihydroxybiphenyl,** prepared from the dihydroxy compound and *p*-toluenesulfonyl chloride, melted at 198–199°.

Anal. Calcd. for $C_{19}H_{14}O_4Br_2S$: Br, 32.1. Found: Br, 31.9 and 31.9.

Bromination of 5,5'-Dibromo-2,2'-dihydroxybiphenyl.—To 3.40 g. (0.01 mole) of 5,5'-dibromo-2,2'-dihydroxybiphenyl in 10 cc. of glacial acetic acid was added 22 cc. of a molar solution of bromine in glacial acetic acid. The solution was then refluxed until the bromine color disap-

(9) Perkin and Robinson, *J. Chem. Soc.*, **105**, 2383 (1914).

(10) Praxmarer, *Monatsh.*, **27**, 1204 (1906).

(11) Wittig, Pöckels and Dröge, *Ber.*, **71**, 1903 (1938). An earlier study showed that *n*-butyllithium and *p*-bromoanisole also gave 5-bromo-2-methoxyphenyllithium: Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

peared and the product was precipitated by the addition of water. There was obtained a quantitative yield of compound melting at 188–192°. Two crystallizations from ethanol gave a product melting at 199–200° and a recrystallization from methanol gave a final melting point of 200–201°. A mixed melting point with the tetrabromodihydroxybiphenyl (m. p., 200–201°) prepared directly from 2,2′-dihydroxybiphenyl, according to the directions of Diels and Bibergeil,[1] showed no depression. Accordingly, two of the bromine atoms in the 200–201° melting tetrabromo compound are in the 5,5′-positions. The remaining two bromine atoms are shown, in a subsequent experiment, to be in the 3,3′-positions.

Under corresponding conditions, 5,5′-dibromo-2,2′-dimethoxybiphenyl was not brominated. The starting material was recovered unchanged after being allowed to stand with the calculated quantity of bromine in acetic acid for thirty-six hours and being heated at 80° for two hours.

3,3′,5,5′ - Tetrabromo - 2,2′ - dimethoxybiphenyl.—The tetrabromo-2,2′-dihydroxybiphenyl, prepared according to the directions of Diels and Bibergeil,[1] melting at 200–201°, was quantitatively methylated by treatment with methyl sulfate and alkali to yield a product which melted at 84–85° after crystallization from ethanol. Recrystallization from methanol raised the melting point to 86–87°.

Anal. Calcd. for $C_{14}H_{10}O_2Br_4$: methoxyl, 11.7. Found: methoxyl, 11.5.

Tetrabromo-2,2′-dimethoxybiphenyl with Phenyllithium.—To 0.012 mole of phenyllithium in 50 cc. of ether was added with stirring 3.18 g. (0.006 mole) of the tetrabromo-2,2′-dimethoxybiphenyl. The bromo compound went into solution and a few seconds later a white precipitate began to appear. This precipitate became very thick so an additional 50 cc. of ether was added. After one hour of stirring the mixture was carbonated by pouring it upon crushed solid carbon dioxide and there was obtained 1.7 g. (72.6%) of crude acid which melted at 220–230°. Four recrystallizations from glacial acetic acid gave 0.3 g. (12.8%) of white crystalline **2,2′-dimethoxy-5,5′-dibromo-3,3′-biphenyldicarboxylic acid** which sintered at 265° and melted at 274–275° with decomposition.

Anal. Calcd. for $C_{16}H_{12}O_6Br_2$: methoxyl, 13.48. Found: methoxyl, 13.58.

Fifty milligrams of the bromo-acid was dehalogenated by shaking for one hour with one-half gram of palladium–calcium carbonate catalyst in 15 cc. of ethanol under 3 atmospheres of hydrogen. There was obtained 25 mg. of acid melting at 203–206°. Recrystallization from dilute ethanol raised the melting point to 207° and a mixed melting point with authentic 2,2′-dimethoxy-3,3′-biphenyldicarboxylic acid (m. p. 208–209°) showed no depression. Accordingly, the remaining two bromine atoms in the tetrabromo compound are in the 3,3′-positions.

The authors are grateful to Mr. H. B. Willis for assistance with some of the analyses.

Summary

Halogen–metal and hydrogen-metal interconversion reactions by organolithium compounds have been used to establish the structures of some derivatives of 2,2′-dihydroxybiphenyl. These biphenyl compounds were examined incidental to studies on the preparation of difficultly accessible dibenzofurans from derivatives of 2,2′-dihydroxybiphenyl by ring closure reactions.

AMES, IOWA RECEIVED MAY 29, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

Nitrogen Compounds in Petroleum Distillates. XVIII. Isolation, Ozonization and Synthesis of 2,4-Dimethyl-8-s-butylquinoline

BY LESLIE M. SCHENCK AND J. R. BAILEY

Introduction

2,3,4-Trimethyl-8-ethylquinoline and 2,3,4-trimethyl-8-*n*-propylquinoline have been isolated from the 320–330° kero base fraction[1] by the employment of cumulative extraction[2] and multiple acid extraction[3] in their segregation.

In order to compare the efficiency of multiple acid extraction and counter-current extraction the authors have reworked the residual material from which the above bases were separated. The original base fractions are listed in Tables II and III of a previous paper.[1] The residual bases were processed through cumulative extraction, followed by counter-current extraction. The column used is a semi-automatic modification of the original designed by Schutze, Quebedeaux and Lochte.[4] The efficiency of the modified column is more than fifteen theoretical plates in separation of acetic acid from water with methyl isobutyl ketone the solvent medium, when plotted according to the method described by Varteressian and Fenske.[5]

(1) This material was furnished the Texas Laboratory by the Union Oil Company of California. Schenck and Bailey, THIS JOURNAL, **61**, 2613 (1939).

(2) Perrin and Bailey, *ibid.*, **55**, 4136 (1933).

(3) *Cf.* Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1938, p. 200.

(4) Schutze, Quebedeaux and Lochte, *Ind. Eng. Chem., Anal. Ed.*, **10**, 676 (1938).

(5) Varteressian and Fenske, *Ind. Eng. Chem.*, **28**, 1353 (1936). The efficiency of the column was tested by Ney; unpublished observation by William O. Ney, Jr., Texas Laboratory.