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Synthesis of Ten New Diphenoxybiphenyls

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Ten new diphenoxybiphenyls were synthesized utilizing the Ullmann condensation reaction so that all 12 possible isomers are known. Percent yields, physical properties, and thermal stabilities are given. Although all isomers have equivalent thermal stabilities, for application as heat transfer or hydraulic fluids, the isomers containing meta links give the widest liquid range.

The use of diphenyl ether as a heat transfer fluid at temperatures up to 700–800°F. in pressurized systems is well established. In unpressurized systems, however, no organic fluids for this temperature range were available at suitable costs until the diphenoxybiphenyls (*10*) and the phenoxyphenoxybiphenyls (*11*) were reported for this application.

To evaluate these related aryl ethers on a cost-performance basis as heat transfer fluids at 800°F, we prepared all of the 12 diphenoxybiphenyl isomers of which 10 are new. To our knowledge this is the first complete set of disubstituted biphenyl derivatives.

The diphenoxybiphenyls were prepared either by the Ullmann condensation (*14*, *19*, *20*) or the Ullmann biphenyl coupling reaction (*9*). The mechanism and parameters of the Ullmann condensation have been studied in detail by a number of workers (*4*, *5*, *23–25*). It has been used recently for the synthesis of seven new polyphenyl ethers containing the biphenyl unit as the central moiety (*12*).

Since the Ullmann condensation is the most general method for the formation of diaryl ether links, this reaction was also used to prepare aminophenyl phenyl ethers directly from chloroanilines. These latter compounds were easily diazotized to key intermediate iodophenyl phenyl ethers and utilized as depicted in Schemes C and D.

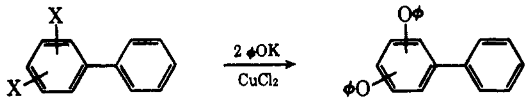
The Ullmann coupling reaction was used to obtain not only symmetrical dichlorobiphenyls having one chlorine in each ring, but also to obtain key intermediate chlorophenoxybiphenyls. The marked difference in reactivity of aryl iodides as compared to aryl chlorides allowed us to obtain chlorophenoxybiphenyl intermediates from Ullmann coupling reaction mixtures. The differences in physical properties of the reaction products allowed us to obtain separable mixtures via prior selection of reactants.

Monochlorobiphenyls and dichlorobiphenyls containing chlorines in the same ring of the biphenyl nucleus were prepared by the Gomberg reaction.

The reaction schemes A and B used for the diphenoxybiphenyls involve the choice either of reaction between a *x,x*-dichlorobiphenyl and potassium phenate or of reaction between *x,x'*-dichlorobiphenyls and potassium phenate. Reaction schemes C and D used for the diphenoxybiphenyls involve the choice of the Ullmann coupling reaction leading to either symmetrical diphenoxybiphenyls or chlorophenoxybiphenyls, easily converted to unsymmetrical diphenoxybiphenyls using potassium phenate.

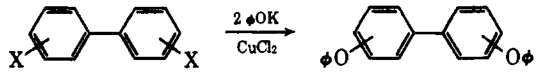
While copper is the standard catalyst for the synthesis of ethers from aryl bromides, cupric chloride was found to be more effective with aryl chlorides. With this catalyst the diphenoxybiphenyls listed in Table I were obtained in a range of 50–87% yield (68% average yield) from the aryl halides. The average yield for the six isomers prepared via scheme A was 74%, for the four isomers prepared via scheme B 71%, and for the two isomers prepared via scheme D 80%. Gas-liquid chromatography (glc) analyses of each compound showed their purity to be

Scheme A:



(I, II, III, IV, V, and VI)

Scheme B:



(VII, VIII, IX and X)

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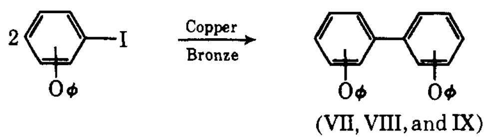
Table I. Synthesis and Properties of Diphenoxybiphenyls

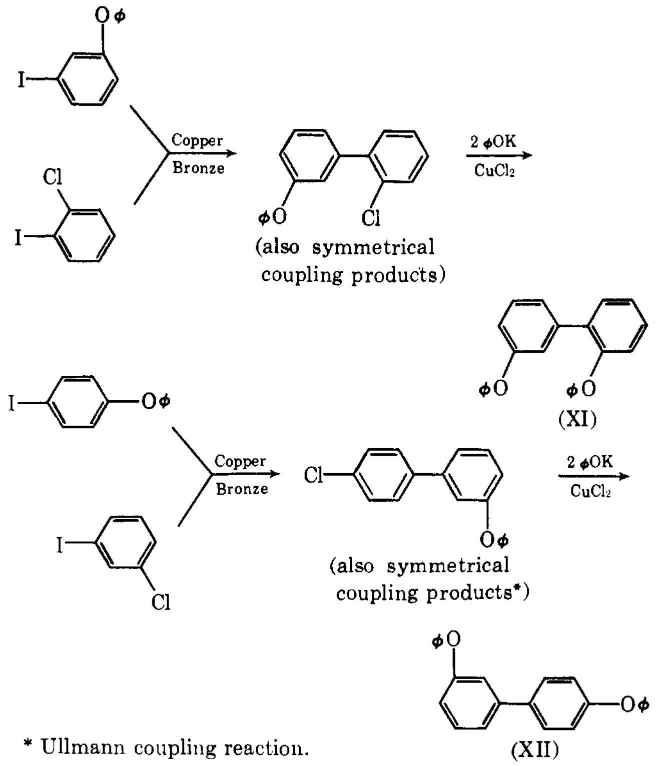
		Starting Materials										
Compound[a]	Scheme	KOH, moles	Phenol, moles	Aryl halide	Mole	Time, hr	Temp., °C	Yield, %	Mp, °C	Bp, °C/mm	n^{25}_{D}	T_D, °F
I 2,3-Diphenoxybiphenyl	A	1.0	2.6	2,3-Dichlorobiphenyl (*6*)	0.16	12	195	54	92	192–5/0.35		815
II 2,4-Diphenoxybiphenyl	A	1.0	2.6	2,4-Dichlorobiphenyl (*7*)	0.15	12	200	81	78	194–201/0.4		817
III 2,5-Diphenoxybiphenyl	A	1.0	2.6	2,5-Dichlorobiphenyl (*15*)	0.16	12	195	77	94–5	205–6/0.4		822
IV 2,6-Diphenoxybiphenyl	A	1.5	2.6	2,6-Dichlorobiphenyl	0.15	16	190	71	82	178–84/0.05		816
V 3,4-Diphenoxybiphenyl	A	1.0	2.6	3,4-Dichlorobiphenyl (*2*)	0.15	12	195	80	...	205–10/0.35	1.6478	809
VI 3,5-Diphenoxybiphenyl	A	1.0	2.6	3,5-Dichlorobiphenyl (*15*)	0.17	12	190	83	92–3	214–15/0.4		837
VII 2,2′-Diphenoxybiphenyl (*13*)	B,C	1.0	2.6	2,2′-Dichlorobiphenyl (*8*)	0.11	12	185	79	100–01	182–4/0.3		844
VIII 3,3′-Diphenoxybiphenyl	B,C	1.0	2.6	3,3′-Dichlorobiphenyl (*16*)	0.13	12	195	84	...	211–14/0.35	1.6428	838
IX 4,4′-Diphenoxybiphenyl (*21*)	B,C	1.5	3.2	4,4′-Dichlorobiphenyl (*16*)	0.5	12	200	50	155			826
X 2,4′-Diphenoxybiphenyl	B	1.5	2.6	2,4′-Dichlorobiphenyl (*6*)	0.45	12	195	87	67–8	205–11/0.45		844
XI 2,3′-Diphenoxybiphenyl	D	1.0	2.6	2-Chloro-3′-phenoxybiphenyl	0.16	16	190	76	...	220–2/0.65	1.6385	822
XII 3,4′-Diphenoxybiphenyl	D	1.0	2.6	3-Chloro-4′-phenoxybiphenyl	0.16	16	190	85	...	222–4/0.25	1.6480	838

[a] Elemental analyses (C,H) in agreement with theoretical values have been obtained and submitted for review.

Scheme C:



Scheme D:



* Ullmann coupling reaction.

greater than 99%. Since some reductive dehalogenation generally occurs to a minor extent in all copper-catalyzed Ullmann reactions (5% minimum), the moderately high yields (68%) and high purity of diphenoxybiphenyls obtained were quite satisfactory for this study.

The thermal stabilities of all the diphenoxybiphenyls as determined by the decomposition point fell within experimental error in the range 809–844°F indicating that orientation has no influence on this property. As expected the melting points varied widely and as in the case with the bis(x-phenoxyphenyl) ethers the meta isomers were the lowest melting. 3,3′-Diphenoxybiphenyl, the analog of bis(3-phenoxyphenyl) ether which is the lowest melting bis(x-phenoxyphenyl) ether, did not crystallize. Two analogs of 2-phenoxyphenyl-3′-phenoxyphenyl ether (75–76°C) and 3-phenoxyphenyl-4′-phenoxyphenyl ether (76°C), namely 2,3′-diphenoxybiphenyl and 3,4′-diphenoxybiphenyl, were liquids at room temperature. Thus the three diphenoxybiphenyls previously mentioned and 3,4-diphenoxybiphenyl would be the most desirable compounds for heat transfer or hydraulic fluid applications.

Reaction conditions, ratio of reactants, and physical properties of the diphenoxybiphenyls are listed in Table I. Excess potassium phenate was used over the halide to "force" reaction. Examination of the data from this study does not suggest any optimum level of phenate to halide.

EXPERIMENTAL

All boiling points and melting points are uncorrected. Microanalyses were performed by Gailbraith Laboratories, Inc., Knoxville, Tenn. Analytical gas-liquid chromatograms were determined using an F and M 720 dual column gas chromatograph. The dual columns were 20 ft, 0.25 o.d. packed with 12% Dow Corning High Vacuum grease dispersed on 45–50 mesh Chromosorb P. Column temperatures were generally in the range of 250–75°C using a helium flow of 70 ml/min. Sample sizes of 0.1 μl. were used at maximum attenuation to obtain optimum resolution and detection of any trace impurities for the compounds in the $C_{24}H_{18}O_2$ molecular-weight range reported herein. Our standard for thermal stability is the "decomposition point," previously defined as the temperature in °F at which a compound decomposes so as to give an isothermal rate of pressure rise of 0.014 mm of Hg/sec (*1*).

The chloro- and dichloroanilines and chloroiodobenzenes used in these studies were purchased and analyzed by glc (99%). For the monochlorobiphenyls and the dichlorobiphenyls used in these studies, one typical example of each synthetic method will be given.

2,6-Dichlorobiphenyl. 2,6-Dichloroaniline (113 grams, 0.7 mole) was added to 188 ml of concentrated hydrochloric acid and 188 ml of water at ice-bath temperatures. Sodium nitrite (48.5 grams, 0.7 mole) dissolved in 200 ml of water was added to the amine slurry at ice-bath temperatures. After the addition of sodium nitrite solution the mixture was stirred for 0.5 hr, filtered through glass wool, and the chilled diazonium salt solution was added to 1 liter of chilled benzene. A solution of sodium acetate–trihydrate (226 g/750 ml of water) was added at ice-bath temperatures with no noticeable exothermic reaction. These reactants were stirred for 24 hr and allowed to warm to room temperature, then filtered through Hyflo Super Cel, and the organics were washed with excess water until neutral to Congo Red and then were dried ($MgSO_4$). Distillation through a Todd column gave a 35% yield, bp 105–15°C/0.04–0.07 mm, $n^{25}D$ 1.6080, of 2,6-dichlorobiphenyl. *Anal.* Calcd for $C_{12}H_8Cl_2$: C, 64.6; H, 3.61; Cl, 31.8. Found: C, 64.8; H, 3.93; Cl, 31.4. All of the other chloro- and dichlorobiphenyls prepared via the Gomberg reaction were obtained in yields ranging from 30–64% using this procedure. The physical properties of these chloro- and dichlorobiphenyls corresponded with those previously listed in the literature. Glc analyses gave purities greater than 99%.

3,3′-Dichlorobiphenyl. *m*-Chloroiodobenzene (150 grams, 0.63 mole) was heated to 230°C and copper bronze (150 grams, 2.4 moles) added in 30-gram lots over a 2-hr period. The reaction mixture was stirred for 3 hr at 230–50°C, cooled, and treated with excess benzene. The resulting slurry was filtered through Hyflo Super Cel, the filtrate was dried ($MgSO_4$), and excess benzene was removed in vacuo. Distillation through an 18-in. Vigreux column gave a 64% yield, bp 135–40°C/1.0 mm, $n^{25}D$ 1.6254 (*16*). Similarly 2,2′-dichlorobiphenyl and 4,4′-dichlorobiphenyl were prepared in 53 and 48% yields, respectively, and their physical properties agreed satisfactorily with those listed in the literature.

2,4′-Dichlorobiphenyl. This intermediate was prepared in high purity (99% glc) by the chlorination of biphenyl and fractionation employing an Oldershaw column (*22*), mp 45.5°C. Lit. mp 46°C (*6*).

A typical procedure for the preparation of the aminophenylphenyl ethers in these studies was the following:

3-Aminophenylphenyl Ether. This intermediate was prepared from *m*-chloroaniline (564 grams, 4.4 moles), phenol (900 grams, 9.6 moles), potassium hydroxide (336 grams, 6.0 moles), and copper powder (12 grams) via an Ullmann reaction. The reactants were refluxed for 8 hr at 200°C, cooled, taken up in excess benzene, and filtered through Hyflo Super Cel. The organics were washed with excess 1.5*N* potassium hydroxide, dried ($MgSO_4$), and concentrated in vacuo. Distillation through a Todd column gave an 80% yield, bp 120–30°C/0.35 mm, $n^{25}D$ 1.6206 (*18*). 2-Aminophenylphenyl ether and 4-aminophenylphenyl ether were prepared in 63 and 54% yields, respectively. The melting points of these two intermediates agreed with literature values, 44°C for 2-amino and 82°C for the 4-amino derivative. Lit. mp 42.5–43°C (*17*) and 83.5°C (*18*), respectively.

A typical procedure for the preparation of iodophenylphenyl ethers used in these studies was the following: 3-Aminophenylphenyl ether (120 grams, 0.65 mole) was converted to the diazonium chloride at ice-bath temperatures with stirring by addition of the amine to a mixture of 165 ml of concentrated hydrochloric acid and 165 ml of water, followed by the addition of sodium nitrite (48 grams, 0.58 mole) dissolved in 225 ml over a 1-hr period (5–10°C). A solution of potassium iodide (108 grams, 0.65 mol/120 ml of water) was added gradually over 0.5 hr to this mixture (5–10°C), and the reaction mixture was allowed to warm to room temperature overnight. This mixture was extracted with hexane, the hexane extracts were washed with 3*N* hydrochloric acid and 3*N* potassium hydroxide, and the extracts dried ($MgSO_4$). Distillation through an 18-in. Vigreux column gave a 70% yield, bp 112–18°C/0.25 mm, $n^{25}D$ 1.6362 (*3*). 2-*Iodophenylphenyl ether and 4-iodophenylphenyl* ether were prepared in 72 and 56% yields, respectively. The melting points of these two intermediates agreed with literature values, 56°C for 2-iodo and 46°C for the 4-iodo derivative. Lit. mp 56°C (*3*) and 46°C (*3*), respectively.

2,4-Diphenoxybiphenyl—II (Scheme A). A mixture of phenol (250 grams, 2.66 moles), potassium hydroxide (56 grams, 1 mole) and toluene (25 ml) was heated at 130°C. After all of the water had been azeotroped off, the potassium phenate–phenol melt was heated to 170°C and cupric chloride dihydrate (5 grams) added. 2,4-Dichlorobiphenyl (32.6 grams, 0.146 mole) was next added to the reaction mixture over 0.5 hr and a vigorous reaction ensued (200°C). The reactants were heated for 12 hr at 200°C with stirring, cooled, and dissolved in excess benzene and 3*N* potassium hydroxide. The resulting heterogeneous mixture was filtered through Hyflo Super Cel, the organic layer separated, washed with excess 1.5*N* potassium hydroxide, and dried ($MgSO_4$). Distillation through an 18-in. Vigreux column gave, after collection of less than 10 grams of forerun, an 81% yield of II, bp 194–201°C/0.4 mm, mp 78°C. Compounds I, III, IV, V, and VI were prepared using essentially the same reaction conditions, the appropriate dichlorobiphenyl and potassium phenate (Table I).

3,3′-Diphenoxybiphenyl—VIII (Scheme B). A mixture of phenol (250 grams, 2.66 moles), potassium hydroxide (56 grams, 1 mole), and toluene (25 ml) was heated at 130°C. After all of the water had been azeotroped off, the potassium phenate–phenol melt was heated to 170°C, and cupric chloride dihydrate (5 grams) added. 3,3′-Dichlorobiphenyl (29 grams, 0.13 mole) was next added to the reaction mixture over 0.5 hr, and a vigorous reaction ensued (200°C). The reactants were heated for 12 hr at 195–200°C with stirring, cooled, and dissolved in excess benzene and 3*N* potassium hydroxide. The resulting heterogeneous mixture was filtered through Hyflo Super Cel, the organic layer separated, washed with excess 1.5*N* potassium hydroxide, and dried ($MgSO_4$). Distillation through an 18-in. Vigreux column gave, after collection of less than 10 grams of forerun, an 84% yield of VIII, bp 211–14°C/0.35 mm. Compounds VII, IX, and X were prepared using essentially the same reaction conditions, the appropriate dichlorobiphenyl and potassium phenate (Table I).

3,3′-Diphenoxybiphenyl—VIII (Scheme C). 3-Iodophenylphenyl ether (130 grams, 0.44 mole) was heated to 210°C, and copper bronze (100 grams) was added gradually over 1 hr with stirring. During these additions of copper bronze, the reaction temperatures would rise 15–20°C, indicative of a rapid exothermic coupling. After all of the copper bronze had been added, the reaction mixture was heated to 260–70°C with stirring for 2 hr. The mixture was washed with benzene, filtered through Hyflo Super Cel, and the excess benzene removed in vacuo. The residual materials were distilled through an 18-in. Vigreux column to give, after collection of less than 15 grams of forerun, a 68% yield of VIII, bp 205–11°C/0.15 mm. *Anal.* Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.00; H, 5.54. Compound VII was prepared using essentially the same conditions and 2-iodophenylphenyl ether and copper bronze (75% yield). Compound IX was prepared in 45% yield using essentially the same mode of addition of copper bronze to 4-iodophenylphenyl ether in dimethylformamide (DMF). The lower yields might be due to the necessity for higher reaction temperatures than DMF reflux.

2,3′-Diphenoxybiphenyl—XI (Scheme D). 3-Iodophenylphenyl ether (174.4 grams, 0.59 mole), *o*-chloroiodobenzene (140 grams, 0.59 mole), and copper bronze (315 grams) were heated for a total of 4 hr at 210°C with stirring. During the first additions of copper bronze to the reaction mixture, noticeable exothermic rises occurred. The copper bronze additions were made in 50-gram lots at 15-min intervals. The reaction mixture was taken up in excess benzene, filtered through Hyflo Super Cel, and the copper bronze was washed with benzene. The filtrate was dried ($MgSO_4$), the excess benzene removed in vacuo, and the residue distilled under vacuum through an 18-in, Vigreux column. A forerun of 2,2′-dichlorobiphenyl (58.6 grams) was obtained before the desired 2-chloro-3′-phenoxybiphenyl (32.9 grams, 19% yield), bp 186–92°C/1.1 mm, n^{25}D 1.6255, was obtained. *Anal.* Calcd for $C_{18}H_{13}ClO$: C, 77.0; H, 4.66; Cl, 12.6. Found: C, 77.4; H, 4.80; Cl, 12.3. A higher boiling fraction, 3,3′-diphenoxybiphenyl, bp 210–25°C/0.8 mm, 44 grams, was easily separated from the desired 2-chloro-3′-phenoxybiphenyl via the aforementioned fractional distillation. A mixture of phenol (250 grams, 2.66 moles), potassium hydroxide (56 grams, 1 mole), and toluene (25 ml) was heated at 130°C. After all of the water had been azeotroped off, the potassium phenate–phenol melt was heated to 170°C and cupric chloride dihydrate (5 grams) was added. 2-Chloro-3′-phenoxybiphenyl (43.3 grams, 0.16 mole) was next added to the reaction mixture over a 15-min period. The reactants were heated for 16 hr at 190°C with stirring, cooled, and dissolved in excess benzene and 3*N* potassium hydroxide. The resulting heterogeneous mixture was filtered through Hyflo Super Cel, the organic layer separated, washed with excess 1.5*N* potassium hydroxide, and dried ($MgSO_4$). Distillation through an 18-in. Vigreux column gave, after collection of less than 10 grams of forerun, a 76% yield of XI, bp 220–2°C/0.65 mm.

3,4′-Diphenoxybiphenyl—XII (Scheme D). 4-Iodophenylphenyl ether (280 grams, 0.94 mole), *m*-chloroiodobenzene (238 grams, 1 mole), and copper bronze (500 grams, 7.9 moles) were refluxed for 4 hr at 210°C with stirring. During the first additions of copper bronze to the reaction mixture, noticeable exothermic rises occurred. The copper bronze additions were made in 50-gram lots at 15-min intervals. The warm reaction mixture was dissolved in excess benzene and filtered through Hyflo Super Cel. The "caked" bronze and collected bronze were agitated in a Waring Blendor with excess benzene and again filtered through Hyflo Super Cel. The benzene filtrates were combined and dried ($MgSO_4$), and the excess benzene was removed in vacuo. During the concentration of the benzene extracts, 40 grams of crude 4,4′-diphenoxybiphenyl was collected by filtration. The concentrated residue was distilled under vacuum through an 18-in. Vigreux column and a forerun of 3,3′-dichlorobiphenyl (46.2 grams), bp 100–20°C/0.15 mm, was collected. The desired intermediate, 3-chloro-4′-phenoxybiphenyl, was collected as the center cut boiling principally at 196–9°C/0.5 mm in 36.8% yield (97 grams), mp 41–2°C. *Anal.* Calcd for $C_{18}H_{13}ClO$: C, 77.0; H, 4.66; Cl, 12.6. Found: C, 77.4; H, 4.91; Cl, 12.3. A higher boiling fraction (29 grams), bp 200–38°C/0.15 mm, was identified as crude 4,4′-diphenoxybiphenyl (mp 148–9°C). A mixture of phenol (250 grams, 2.66 moles), potassium hydroxide (56 grams, 1.0 mole), and toluene (25 ml) was heated to 130°C. After all of the water had been azeotroped off, the potassium phenate–phenol melt was heated to 170°C and cupric chloride dihydrate (5 grams) added. 3-Chloro-4′-phenoxybiphenyl (45.8 grams, 0.163 mole) was next added to the reaction mixture over a 15-min period. The reactants were heated for 16 hr at 190°C with stirring, cooled, and dissolved in excess benzene and 3*N* potassium hydroxide. The resulting heterogeneous mixture was filtered through Hyflo Super Cel, the organic layer was separated, washed with excess 1.5*N* potassium hydroxide, and dried ($MgSO_4$). Distillation through an 18-in. Vigreux column gave, after collection of less than 10 grams of forerun, an 85% yield of XII, bp 222–4°C/0.25 mm, n^{25}D 1.6480.

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