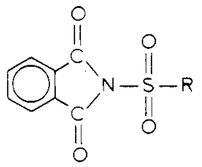
Table I. *N*-Alkyl- and *N*-Arylsulfonylphthalimides



R	Recryst. Solvent[a]	Yield, %[b]	M.P., ° C.	Analysis, % N Calcd.	Analysis, % N Found	Analysis, % S Calcd.	Analysis, % S Found
Methyl	*A*	62	229.5–30	6.22	6.26	14.24	14.27
Ethyl	*B*	65	181.5–82	5.85	5.86	13.40	13.55
n-Propyl	*C*	62	139–39.5	5.53	5.51	12.66	12.69
n-Butyl	*C*	60	114.5–15	5.24	5.27	12.00	11.92
Phenyl	*D*	74	202.5–03.5[c]				
p-Tolyl	*E*	75	239–40[d]				
p-Bromophenyl	*E*	70	247–48[e]				
β-Naphthyl	*E*	73	218–19[f]				

[a] *A*, acetonitrile; *B*, acetonitrile-benzene; *C*, benzene; *D*, toluene; *E*, xylenes (b.p. 135–40° C.). [b] Yields are for purified products. [c] Lit. (*2*) m.p. 205° C. [d] Lit. (*2*) m.p. 237° C. [e] Lit. (*2*) m.p. 246° C. [f] Lit. (*2*) m.p. 216° C.

Reaction of Potassium Phthalimide with Sulfonyl Chlorides. All of the compounds listed in Table I were prepared in the same manner. A stirred mixture of 0.0050 mole of potassium phthalimide and 0.0050 mole of the appropriate sulfonyl chloride in 20 ml. of acetonitrile was heated under reflux for 1 hour. After cooling to ambient temperature, the mixture was poured into 100 ml. of cold water. The white solid, which separated immediately, was removed by filtration, washed with water, and dried. The crude products were purified by one or two recrystallizations from the solvents indicated in Table I.

Each *N*-substituted phthalimide was found to be identical with an authentic sample, which was prepared by the reaction of the appropriate sulfonamide with phthaloyl chloride according to the method of Evans and Dehn (*1*), by mixture melting point determination and infrared spectra comparison.

In experiments that involved methane- and butane-1-sulfonyl chlorides, small amounts of a solid—32 and 20 mg., respectively—precipitated from the aqueous filtrates on standing overnight. This solid was identified by mixture melting point determination and infrared spectra comparison as phthalimide.

ACKNOWLEDGMENT

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Synthesis of Seven New Polyphenyl Ethers

WILLIAM C. HAMMANN and ROBERT M. SCHISLA
Monsanto Co., St. Louis, Mo. 63166
JOHN S. ADAMS, JR.,[1] and STANLEY D. KOCH[1]
Monsanto Research Corp., Dayton Laboratory, Dayton, Ohio 45407

Seven new polyphenyl ethers were synthesized, using a modified Ullmann reaction. Per cent yields, physical properties, and elemental analyses are given.

POLYPHENYL ethers show excellent thermal stability and are used as high-temperature functional fluids, finding application as heat transfer agents. In addition, they have proved useful as the liquid phase in high-temperature chromatographic work (*3*-*5*, *7*). Seven new polyphenyl ethers containing a biphenyl central core were synthesized in these laboratories. The synthetic routes used were similar in each case and involved a modified Ullmann reaction. The mechanism and parameters of this reaction have been studied in detail by a number of workers (*1*, *2*, *8*, *9*). The reaction schemes leading to each compound are depicted below:

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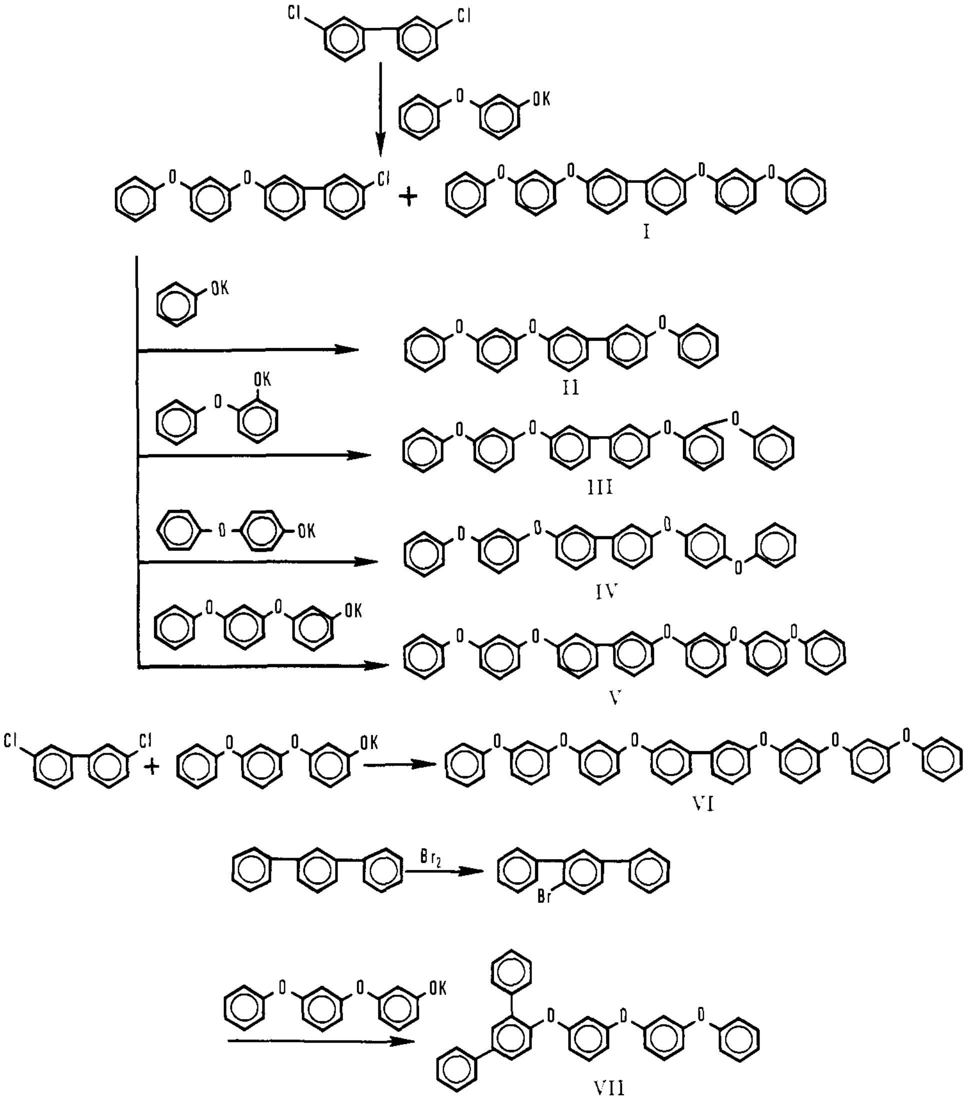
[1] Present address, Horizons Research, Inc., Cleveland, Ohio 44104



EXPERIMENTAL

The phenols used in the syntheses were obtained from Monsanto Co.'s Central Research Department, and were used without further purification. Santowax-M, also obtained from Monsanto Co., was used as received in the preparation of 4′-bromo-*m*-terphenyl, intermediate for VII, 4′-[*m*-(*m*-phenoxyphenoxy)phenoxy]-*m*-terphenyl. Monsanto Co. also supplied the key intermediate 3,3′-dichlorobiphenyl used in six of the seven syntheses. As received, it was 87% pure, and was further purified by careful fractionation through a 90-cm Vigreux column, followed by topping this distillate, to give 200 grams of 98.7% pure material, considered suitable for synthetic use. The major impurity was 3-chlorobiphenyl.

3,3′-Bis(*m*-phenoxyphenoxy)biphenyl (I) and Key Intermediate, 3-Chloro-3′-(*m*-phenoxyphenoxy)biphenyl. A 500-ml four-necked flask equipped with stirrer, thermometer, and Dean-Stark trap surmounted by a Friedrichs condenser was charged with 93.5 grams (0.505 mole) of *m*-phenoxyphenol, and 30.8 grams (0.50 mole) of potassium hydroxide (assumed in all reactions to be 91% pure) was added in increments with stirring at 100° C. After the initial exothermic reaction had subsided, 80 ml of toluene was added, and water was azeotroped from the reaction mixture until the theoretical amount had been collected, including that from the potassium hydroxide.

The toluene was distilled from the reaction mixture until the pot temperature reached 230° C. After cooling to 150° C., 100 ml of diglyme was added, together with 7 grams of cuprous chloride and 2 grams of copper powder. The reaction mixture was then heated with stirring to 170° C., and 129.3 grams (0.57 mole) of 3,3′-dichlorobiphenyl was added over a 1-hour period. Diglyme was distilled from the reaction mixture until the pot temperature reached 235° C., when reaction was continued for 18 hours. On cooling, the reaction mixture was diluted with an equal volume of ether, and filtered to remove copper and potassium salts. The ethereal solution was washed three times with 150-ml portions of 20% potassium hydroxide, followed by water washing until neutral. The water and potassium hydroxide layers were extracted with additional ether. The ether solutions were combined and dried over anhydrous magnesium sulfate. After filtration and removal of ether on the rotary evaporator, the dark red-brown oil was distilled to yield 47.2 grams of starting 3,3′-dichlorobiphenyl, bp 112–14° C./0.05 mm; 6.2 grams of intermediate fractions, bp 127–202° C./0.03 mm; 71.4 grams (38%) of 3-chloro-3′-(*m*-phenoxyphenoxy)biphenyl, bp 220–2° C./0.04 mm; 20.4 grams of intermediate cuts, bp 223–302° C./0.06 mm; and 17.2 grams of 3,3′-bis(*m*-phenoxyphenoxy)biphenyl (I), bp 312° C./0.05 mm. A pot residue of 8.9 grams remained. Final purification of I was effected by dissolving it in ethyl ether and treating it with 1.0 gram of activated charcoal, followed by filtration through filter aid, removal of ethyl ether on the rotary evaporator, and prolonged treatment in a vacuum oven at 100–10° C./0.1 mm.

3-(*m*-Phenoxyphenoxy)-3′-(*p*-phenoxyphenoxy)biphenyl(IV). This preparation is typical of the syntheses leading to the other three polyphenyl ethers using the same key chloro-

Table I. Yields, Physical Properties, and Elemental Analyses of Polyphenyl Ethers

Compound	% Yield	BP, ° C./Mm.	MP, ° C.	n_D^{25}	d_4^{24}	Analysis {Calcd. / Found} C	H
I	13[a]	312/0.05	85–88	1.6520	...	82.7	5.0
						82.4	5.2
II	56[a]	248–53/0.06	...	1.6474	1.184	83.7	5.2
						83.2	5.2
III	61[a]	255–60/0.02	...	1.6480	1.197	82.7	5.0
						83.0	5.3
IV	62[a]	302–07/0.05	...	1.6500	1.201	82.7	5.0
						82.5	5.1
V	75[a]	340/0.05	...	1.6510	1.219	82.0	4.9
						81.8	5.0
VI	25[b]; 15[c]	...	...	1.658(9)	1.231	81.5	4.9
						81.6	5.0
VII	69[a]	337/0.07	...	[d]	1.185	85.2	5.2
						85.4	5.2

[a] Calculated from weight of distilled material. [b] Based on total product recovered. [c] Based on purified product. [d] Could not be determined at 25° C.

phenoxybiphenyl, but varying the phenol. Work-up in every one of the four cases was virtually identical, the products differing only in boiling point and the other intrinsic physical properties given in Table I. Yields for the four compounds varied from 56–75%, also shown in Table I.

A 250-ml reaction flask equipped with stirrer, dropping funnel, thermometer, and Dean-Stark trap surmounted by a Friedrichs condenser was charged with 200 grams (1.07 mole) of *p*-phenoxyphenol, and 34.9 grams (0.567 mole) of potassium hydroxide was added in increments at 90° C. To the resulting melt was added 50 ml of toluene. The theoretical amount of water was azeotroped from the reaction mixture, followed by removal of toluene up to 230° C. On cooling to 150° C., the reaction mixture was diluted with 150 ml of diglyme, and 5.0 grams of cuprous chloride and 1.0 gram of copper powder were added. Over a 45-minute period, 20 grams (0.054 mole) of 3-chloro-3′-(*m*-phenoxyphenoxy)biphenyl in diglyme was added, and the diglyme was removed by distillation. The stirred reaction mixture was heated at 235° C. for 19 hours. On cooling, an equal volume of ether was added and this mixture was centrifuged to remove salts. The ethereal solution was washed with 25% potassium hydroxide solution to remove excess phenol, and with water until neutral. It was then dried over anhydrous magnesium sulfate.

After filtration and concentration to remove ether, the oil obtained was distilled. One unweighted cut, bp 110-297° C./0.05 mm, was taken, followed by 17.5 grams of product, bp 297-302° C./0.05 mm. Final purification of this material was the same as that described above for I.

3,3′-Bis[*m*(*m*-phenoxyphenoxy)phenoxy]biphenyl (VI). A 250-ml four-necked flask, equipped with stirrer, dropping funnel, thermometer, and Dean-Stark trap surmounted by a Friedrichs condenser, was charged with 59.8 grams (0.215 mole) of *m*-(*m*-phenoxyphenoxy)phenol, to which 13.0 grams (0.208 mole) of potassium hydroxide was added at 90° C., followed by addition of 50 ml of toluene. The stirred reaction mixture was heated to azeotrope water, followed by distillation of toluene until the temperature of the reaction mixture reached 230° C. After cooling, 50 ml of diglyme, 2.5 grams of cuprous chloride, 0.5 gram of copper powder, and 20 grams (0.09 mole) of 3,3′-dichlorobiphenyl were added to this mixture over a 30-minute period at 175° C. Diglyme was distilled from the reaction mixture, which was then heated at 230-60° C. for 18 hours. The cooled, very thick, semisolid mass resulting was dissolved in 500 ml of ethyl ether, and the suspended salts were removed by centrifugation. The resulting ethereal solution was washed thoroughly with 10% potassium hydroxide solution and with water until neutral, and was finally dried over anhydrous magnesium sulfate. After concentrating this solution, it was distilled using a 100-ml distilling flask connected to a 25-cm heated Vigreux column with direct take-off head attached to a fraction cutter. A fraction amounting to 7.0 grams, bp 136-293° C./0.06 mm, was obtained initially. The distillant, after cooling, was transferred to a 25-ml "mini-ware" still pot attached to a Claisen head and "mini-ware" fraction cutter. Distillation using a Wood's metal bath on the still pot gave 10 grams of viscous red-orange liquid, bp 348-52° C./0.09 mm, at a pot temperature of 428° C. Elemental analysis showed this cut to be about 80% desired product and 20% of presumably 3-chloro-3′-[*m*-(*m*-phenoxyphenoxy)phenoxy]biphenyl. Since 450° C. would be an upper limit for many of the ethers with regard to accelerated thermal decomposition, it was decided not to attempt to distill the remainder of the pot residue, amounting to 11 grams. Instead, this black glass (at room temperature) was dissolved in 300 ml of ethyl ether, treated with 1 gram of activated charcoal, and filtered through filter aid to give an orange fluorescent solution which, on concentration, gave a dark red-orange viscous liquid. The treatment was repeated, using 125 ml of ethyl ether and 0.5 gram of charcoal. After the ether was removed on the rotary evaporator, the orange liquid was placed in a vacuum oven for 15 hours at 110° C./0.1 mm and finally 1 hour at 125° C./0.1 mm to give 9.8 grams of light orange product. Although not determined, we estimate by extrapolation from the boiling points of the closely related five-, six-, and seven-ring ethers prepared that this eight-ring ether would have bp ~380-90° C./0.05 mm.

4′-[*m*-(*m*-Phenoxyphenoxy)phenoxy]-*m*-terphenyl (VII). Synthesis of 4′-bromo-*m*-terphenyl was carried out by the procedure of Schmidt *et al.* (*6*). Product was purified by preparative vapor phase chromatography, using an F&M Model 775 chromatographic unit, incorporating a 6.5-ft × 4-inch column packed with 20% UCW98 on Chromosorb W. Injection port and dectector temperatures were 340° C., with column temperature at 240° C. The resulting product was calculated to be 99+% pure by vpc.

A 500-ml flask equipped with dropping funnel, stirrer, thermometer, and a Dean-Stark trap surmounted by a Friedrichs condenser was charged with 100 grams (0.36 mole) of *m*(*m*-phenoxyphenoxy)phenol and 9.5 grams of potassium hydroxide. The reaction mixture was heated with stirring until the potassium hydroxide had completely dissolved. Then 250 ml of toluene was added to azeotrope the theoretical amount of water. Toluene was distilled from the system until the temperature reached 200° C. After the temperature of the reaction mixture had returned to 150° C, 100 ml of diglyme was added, together with 2.5 grams of cuprous chloride and 0.5 gram of copper powder.

The temperature was gradually increased to 160° C. and 20.6 grams (0.067 mole) of 4′-bromo-*m*-terphenyl, dissolved in 40 ml of diglyme, was added dropwise. The reaction was allowed to continue for 10 hours at 185° C. It was then diluted with ethyl ether and filtered. The ether layer was washed with 2 × 100 ml of 25% aqueous potassium hydroxide, followed by water washing until neutral. The aqueous washes were extracted with 2 × 100 ml of ethyl ether. The ether layers were combined, washed with distilled water until neutral, dried over magnesium sulfate, and filtered. A brown viscous liquid was obtained upon removal of the ether. This material was distilled to obtain 10 grams of forecut, bp 80–337° C./0.07 mm, and 23.5 grams of 4′-[*m*-(*m*-phenoxyphenoxy)phenoxy]-*m*-terphenyl, bp 337° C./0.07 mm., as a yellow viscous liquid.

Final purification was effected as described above for the other ethers prepared.

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3,3′-Biscoumarins

LLOYD L. WOODS and SAMIR M. SHAMMA
Texas Southern University, Houston, Tex. 77004

Five 3,3′-biscoumarins, none of which have been reported previously, were synthesized by a modification of the Perkin reaction.

A MIXTURE consisting of 0.1 mole of anhydrous powdered potassium succinate and 0.2 mole of the aldehyde was thoroughly mixed with 40 ml. of acetic anhydride in a flask and then heated in a Hi-Temp oil bath, already at equilibrium between 155° and 160° C. for 30 to 45 minutes. The mixtures were diluted with 300 ml. of water, cooled, and filtered and the precipitates dried in air. The compounds were powdered and dried 3 days in a vacuum desiccator over Drierite.

A sample of each compound was purified by extraction with heptane, then ethyl acetate, and finally with boiling ethanol. The samples thus purified gave the analyses and infrared data shown in Table I.

One gram of compound 1 after having been treated as

Table I. Biscoumarins

	Aldehyde Used	M.P., °C.	Yields, %	Formula	Calculated C	Calculated H	Calculated Other	Found C	Found H	Found Other
1.	Salicylaldehyde	328	97	$C_{18}H_{10}O_4$	74.47	3.47		74.55	3.69	
2.	5-Chloro-salicylaldehyde	>360	98	$C_{18}H_8Cl_2O_4$	60.19	2.24	19.74(Cl)	59.89	2.36	19.75(Cl)
3.	3-Methoxy salicylaldehyde	346–348	99	$C_{20}H_{14}O_6$	68.56	4.02		68.36	4.06	
4.	2-Hydroxy-1-naphthaldehyde	>360	97	$C_{26}H_{14}O_4$	79.99	3.61		80.28	3.82	
5.	5-Bromo-salicylaldehyde	>360	100	$C_{18}H_8Br_2O_4$	48.25	1.79	35.66(Br)	48.53	2.01	35.77(Br)

1. 3,3′-Biscoumarin- 1703[a]
2. 6,6′-Dichloro-3,3′-biscoumarin- 1707
3. 8,8′-Dimethoxy-3,3′-biscoumarin- 1707
4. 2,2′-Bis(3*H*-naphtho[2,1-*b*]pyran-3,3′-dione- 1710
5. 6,6′-Dibromo-3,3′-biscoumarin- 1715

[a] Carbonyl absorption of infrared spectrum in cm.$^{-1}$ KBr pellet taken on Beckman IR-8.