Synthesis of n-Alkyl p-Diphenyl Ethers and Aryl p-Diphenyl Ethers

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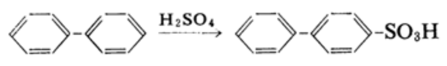
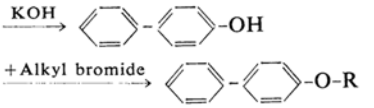
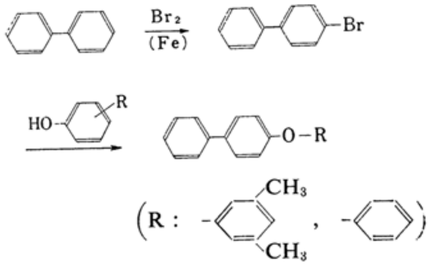
n-Alkyl *p*-diphenyl ethers[1] whose alkyl group consists of either C_1, C_2, C_3, C_4 and C_5, and aryl *p*-diphenyl ethers whose aryl group includes phenyl[2], *p*-tolyl[3] and benzyl[1] have hitherto been reported on in the literature. Their melting points are shown in Tables I and II.

The melting points, except for those of allyl, benzyl and *p*-tolyl ether, are within a relatively narrow range. In order to examine the physical properties of the ethers which have a longer alkyl chain or a methylated benzene ring, the author newly synthesized *n*-alkyl ethers (*n*-C_6, *n*-C_7 and *n*-C_8) and an aryl ether (3, 5-dimethylphenyl) along with the known *n*-amyl and *p*-phenyl ethers by the scheme shown below.



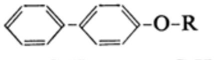


(R : *n*-C_5, *n*-C_6, *n*-C_7, *n*-C_8)



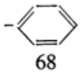
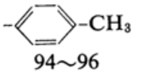
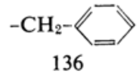
Diphenyl was first sulfonated in nitrobenzene[4], and the resulting sulfonic acid was

TABLE I. ALKYL DIPHENYL ETHERS



R	CH_3	C_2H_5	*n*-C_3H_7	*iso*-C_3H_7	-CH=CH-CH_3	*n*-C_4H_9	*n*-C_5H_{11}
M. p. of the ether, °C	90	76, 78	76～77	73	86	74～75	64～65

TABLE II. ARYL DIPHENYL ETHERS

R			
M. p. of the ether, °C	68	94～96	136

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[1] C. M. Brewster et al., *J. Am. Chem. Soc.*, **61**, 3083 (1939).

[2] A. Luttringkhaus, *Chem. Ber.*, **89**, 463 (1956).

[3] R. L. Huang, *J. Chem. Soc.*, **1954**, 3084.

[4] E. Gebauer-Fülnegg et al., *Monatsh.*, **49**, 41 (1928).

TABLE III

	n-Amyl	*n*-Hexyl	*n*-Heptyl	*n*-Octyl	Phenyl	3, 5-Dimethylphenyl
Appearance	Colorless flakes	Colorless flakes	Colorless flakes	Colorless flakes	Colorless flakes	Colorless needles
B. p., °C/2 mmHg	178.5~179.5	187~188	201~201.3	208		210~213
M. p., °C	64~65	63.5~64.3	70.7~71.7	68~69	67~68	65.5~66.5
Elementary analysis						
C, %	84.88	84.74	85.17	85.26	—	87.74
H, %	8.25	8.46	8.99	9.42	—	6.49
Calculated for	$C_{17}H_{20}O$	$C_{18}H_{22}O$	$C_{19}H_{24}O$	$C_{20}H_{26}O$	—	$C_{20}H_{18}O$
C, %	84.95	84.99	85.02	85.05	—	87.56
H, %	8.39	8.72	9.01	9.28	—	6.61

fused with potassium hydroxide to give *p*-phenylphenol, which was condensed with *n*-alkyl bromide in ethanol in the presence of sodium hydroxide.

In the case of aryl ethers, diphenyl dissolved in carbon tetrachloride was treated with bromine in the presence of iron powder, and the resulting *p*-bromodiphenyl was condensed with phenols in the presence of copper powder.

The properties of the purified specimens are shown in Table III.

Experimental

Materials.—*Diphenyl*[5].—A sample supplied by Yawata Chemical Industry Co. was recrystallized from ethanol in the form of white leaflets, m. p. 68~69.2°C.

n-Octanol[6].—A commercial reagent was redistilled, b. p. 194~196°C, n_D^{25} 1.4266.

n-Amyl Bromide[7].—A commercial reagent was redistilled, b. p. 126.5~128°C (757 mmHg) (uncorr.).

n-Hexyl Bromide[8].—A commercial reagent was redistilled, b. p. 155~157°C (757 mmHg), n_D^{20} 1.4469.

n-Heptyl Bromide[9].—A mixture of *n*-heptyl alcohol (20 g.), 72 g. of hydrobromic acid and 18.2 g. of concentrated sulfuric acid was refluxed for 6 hr., then washed with water and dilute sodium carbonate solution and finally dried over calcium chloride; yield 22.87 g., 75%, n_D^{25} 1.4482.

n-Octyl Bromide[10].—It was prepared in the same manner as above. From a mixture of *n*-octanol (18.6 g.), 65 g. of hydrobromic acid, 17.0 g. of concentrated sulfuric acid, and 9.6 g. of a fraction boiling at 195~203°C were obtained; $n_D^{19.5}$ 1.454.

1, 3, 5-Xylenol[11].—Commercial reagent; m. p. 61°C.

Bromine, Potassium Hydroxide, Sulfuric Acid.—Commercial reagent.

Synthesis of *n*-Alkyl *p*-Diphenyl Ether.—*Sulfonation of Biphenyl.*—Biphenyl (30 g.), 40 cc. of nitrobenzene and 19 g. of concentrated sulfuric acid were kept at 80~90°C while being stirred for 6.5 hr. Unreacted diphenyl and nitrobenzene were steam distilled, and sodium salt of diphenyl-*p*-sulfonic acid (20.7 g.) was obtained by the addition of a sodium hydroxide solution to the residue. 8.1 g. of diphenyl was recovered. The yield of the sulfonic acid based on the consumed diphenyl was about 57%.

Alkali Fusion of the Sulfonate.—Into potassium hydroxide melted in an nickel crucible at 290~300°C the sodium sulfonate was gradually stirred, and the heating was continued for a while. The mixture was then allowed to cool and dissolved in water. Upon the addition of hydrochloric acid to this solution, a precipitate of crude *p*-phenylphenol was obtained. The results of the potassium hydroxide fusion are shown in Table IV.

TABLE IV

Na-sulfonate g.	KOH g.	Time of fusion min. at		*p*-Phenyl-phenol	
		290~300°C	320~330°C	Amount g.	Yield %
7.7	25.0	10	15	4.15	81
12.0	46.5	15	5	6.80	85
9.6	32.0	10	5	5.60	88

The crude phenylphenol was distilled in vacuo to give a distillate which boiled at 184~190°C (18 mmHg) and melted at 159~162°C (uncorr.).

Condensation.—It was carried out by the Williamson reaction. A mixture of *p*-phenylphenol, ethanol, sodium hydroxide and *n*-alkyl bromide was refluxed, and the mixture was poured into water. On the addition of an aqueous solution of sodium hydroxide, the crude ether was separated from the phenylphenol which had been recovered by the acidification of the filtrate. The crude ether was purified by recrystallization from ethanol. The results are shown in Table V.

Synthesis of Aryl *p*-Diphenyl Ether.—*Synthesis of p-Bromodiphenyl*[12].—Bromine (90 g.) was gradually stirred into a mixture of diphenyl (86 g.), 260 cc. of carbon tetrachloride and 2 g. of iron powder, and heating was continued at 45~55°C for 11 hr. The solvent was then distilled off and the

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5) I. Heilbron, "Dictionary of Organic Compounds", Vol. 2, Oxford University Press, New York (1953), p. 401.
6) Ibid., Vol. 4, p. 13.
7) Ibid., Vol. 1, p. 152.
8) Ibid., Vol. 1, p. 329.
9) Ibid., Vol. 1, p. 329.
10) Ibid., Vol. 4, p. 14.
11) Ibid., Vol. 4, p. 680.
12) L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry" (English Ed.), Walter de Gruyter, Berlin (1952), p. 102.

TABLE V

Alkyl	Alkyl-bromide g.	p-Phenyl-phenol g.	NaOH g.	EtOH cc.	Time hr.	Crude ether g.	Recrystallized ether Amount g.	Recrystallized ether Yield %	Recrystallized ether M. p. °C	Mol. wt. Found	Mol. wt. Calcd.
n-Amyl	3.4	3.4	1	33	2	3.9	2.19	46	64～65	236	240
n-Hexyl	3.4	3.4	0.75	30	3	2.4	1.16	23	63～63.5	247	254
〃	4.2	3.4	1	33	2	2.4	0.93	18	63.5～64.3		
n-Heptyl	4.0	3.4	1	40	2	4.1	3.5	66	70.7～71.7	265	268
n-Octyl	5.0	5.0	1.3	52	1	5.1	8.85	53	68～69	283	282
〃	5.0	5.0	1.3	52	2.5	6.0					

residue distilled in vacuo, the distillate was recrystallized to give 66.7 g. of *p*-bromodiphenyl; yield 51%, m. p. 86～88.5°C.

p-Diphenylphenyl Ether.—A mixture of *p*-bromodiphenyl (47 g.), 27 g. of phenol, 12 g. of potassium hydroxide and 2 g. of copper powder was heated at 184～240°C for 6 hr. The mixture was extracted with benzene, and the benzene extract was concentrated and distilled in vacuo. Recrystallization of the distillate yielded 37.5 g. (76%) of the crude ether, m. p. 60～68°C which was further recrystallized from ethanol to give a purified specimen, m. p. 67～68°C.

Synthesis of 3, 5-Dimethylphenyl p-Diphenyl Ether.—A mixture of *p*-bromodiphenyl (8.7 g.), 2.2 g. of potassium hydroxide, 4.78 g. of 1, 3, 5-xylenol and 0.05 g. of copper powder was heated at 160～200°C for 2.5 hr. The mixture, when treated in the usual manner, gave 3.33 g. of colorless flakes; yield 33%, m. p. 65.5～66.5°C.

Found: C, 87.74; H, 6.49. Mol. wt., 273. Calcd. for $C_{20}H_{18}O$: C, 87.56; H, 6.61%. Mol. wt., 274.

Infrared Spectra of the p-Diphenyl Ethers.—The spectra of *n*-alkyl (C_5, C_6, C_7, C_8) and aryl (C_8) ethers are shown in Figs. 1, 2, 3, 4 and 5. The absorption bands common to these ethers are as follows: a band at 8 μ (1250 cm^{-1}) is assigned to the C–O stretching of the ether linkage, and an appearance of a band in the vicinity of 12.05 μ which corresponds to two adjacent hydrogen atoms in the benzene ring shows that the ethers are all substituted at the para position of diphenyl. Also,

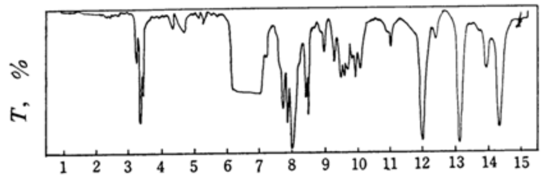

Fig. 1. *n*-Amyl *p*-diphenyl ether.

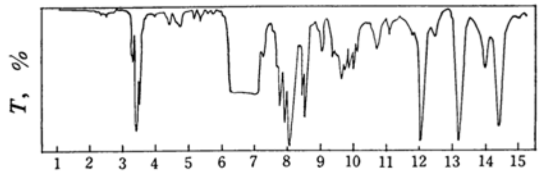

Fig. 2. *n*-Hexyl *p*-diphenyl ether.

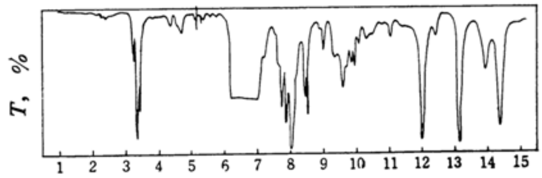

Fig. 3. *n*-Heptyl *p*-diphenyl ether.

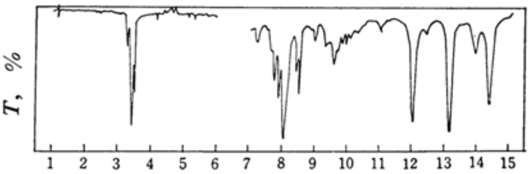

Fig. 4. *n*-Octyl *p*-diphenyl ether.

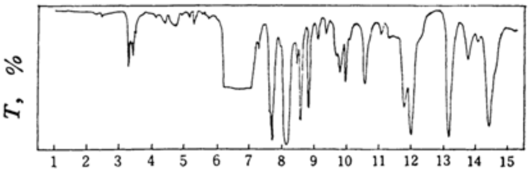

Fig. 5. 3,5-Dimethylphenyl *p*-diphenyl ether.

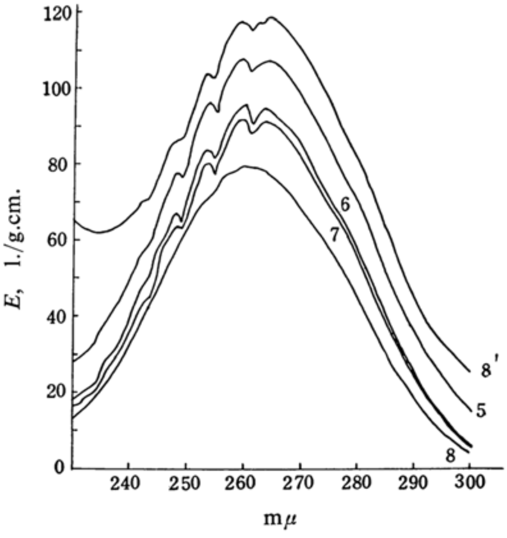

Fig. 6. *p*-Diphenyl ethers.

5; *n*-Amyl (*E*+10) 6; *n*-Hexyl 7; *n*-Heptyl
8; *n*-Octyl 8'; 3,5-Dimethylphenyl (*E*+20)

an absorption band due to the rocking motion of a methylene group in the n-alkyl chain appears at the same wavelength in all the n-alkyl ethers, as is shown below.

No. of C atoms of n-alkyl ether	5	6	7	8
Absorption, μ	13.94	13.95	13.93	13.95

A strong band near 1250 cm^{-1} of the n-alkyl ethers is shifted to a slightly shorter wavelength compared with that of the aryl ethers.

	n-Alkyl ether			
The ethers	n-C_5	n-C_6	n-C_7	n-C_8
Absorption, μ	8.05	8.07	8.06	8.07

	Aryl ether		
The ethers	Phenyl	3, 5-Dimethyl-phenyl	p,p'-Diphenyl
Absorption, μ	8.15	8.20	8.15

Ultraviolet Spectra.—The spectra in cyclohexane are shown in Fig. 6. Showing almost the same pattern, bands appearing at 248, 254, 260 and 264 mμ are common to these ethers, except for n-octyl ether, and the maximum absorption is at a longer wavelength than that of p-diphenyl methyl ether, which has been reported to be 259 mμ in cyclohexane. The absorption maximum of p-terphenyl, which may be regarded as a phenyl derivative of diphenyl, is at 276 mμ in hexane. Thus the introduction of a phenoxyl group, i. e. an ether linkage, to diphenyl is less bathochromic than a phenyl.

Solubility.—The new alkyl ethers (C_6, C_7, C_8) are only with difficulty soluble in cold ethanol but are readily soluble in benzene. 3, 5-Dimethylphenyl ether is with more difficulty soluble in ethanol than n-alkyl ethers but is readily soluble in benzene.

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