Synthesis of Naphthyl p-Tolyl Ethers

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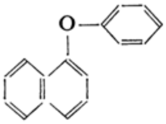
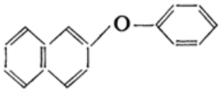
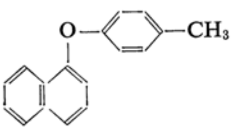
The physical properties of α- and β-naphthyl phenyl ethers (structural formulas I and II) were reported in the literature¹⁾.


(I)
m. p. 54°C
b. p. 349.5°C
(753 mmHg)


(II)
m. p. 45°C
b. p. 335.5°C
(753 mmHg)

In order to examine the physical properties and the thermal stability of aromatic ethers which have a methyl side chain, the author newly synthesized naphthyl *p*-tolyl ethers (formulas III and IV).


(III)

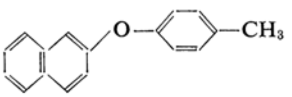

(IV)

TABLE I

Isomer	α-	β-	Calcd.
Appearance	Colorless plates	Colorless needles	
B. p., °C	184∼185 (3 mmHg)	187∼188 (3 mmHg)	
M. p., °C	38∼39	41∼42.3	
Elementary analysis			
C, %	86.96	87.22	87.15
H, %	5.71	6.00	6.02

The properties of purified specimens are shown in Table I.

Paal²⁾ synthesized the β-isomer by a reaction of β-naphthol and potassium nitroso-*p*-tolylsulfamate in benzene and he reported that the compound was red and melted at 135°C. However, the β-isomer which the present author prepared is a white needle and melted at 41∼42.3°C. The melting point of the Paal's compound seems to be too high for the β-isomer in comparison with those of phenoxynaphthalenes and also the red color seems unlikely for a naphthyl tolyl ether structure and it probably be due to some impurities. The

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1) F. Ullmann et al., *Ann.*, **350**, 90 (1906).
2) C. Paal et al., *Ber.*, 30, 884 (1897).

TABLE II. α-NAPHTHYL *p*-TOLYL ETHER

p-Cresol	KOH	α-Bromonaphthalene	Copper	Condition		Main fraction	Crude crystal		
				Temp.	Time		Amount	M. p.	Yield[a)]
g.	g.	g.	g.	°C	hr.	g.	g.	°C	%
16.5	6	20.4	1.0	160~173	4	7.5	4.4	35~38	19
15.8	6	20.7	1.0	220~240	2½	9.2	4.6	37~38	20

a) The yield based on α-bromonaphthalene

TABLE III. β-NAPHTHYL *p*-TOLYL ETHER

β-Naphthol	*p*-Bromotoluene	KOH	Copper	Condition		Crude crystal		
				Temp.	Time	Amount	M. p.	Yield
g.	g.	g.	g.	°C	hr.	g.	°C	%
20	17.5	5.6	2.0	144~150	7	4.55	—	19
14.4	17.1	5.6	2.0	180~200	7	9.25	38~41	39
7.2	9.0	3.0	0.7	200~210	6	4.32	35~39.5	37

physical properties and absorption spectra afford evidence in favor of the compound prepared by the author as the correct β-isomer. In the present experiment, the ethers were synthesized by the Ullmann reaction, that is, the α-isomer from α-bromonaphthalene and *p*-cresol, and the β-isomer from β-naphthol and *p*-bromotoluene.

Experimental

Materials. — *p-Cresol*[3]. — B. p. 200°C (uncorr.), m. p. 32°C.

α-Bromonaphthalene[4].—It was synthesized from naphthalene and bromine in the same manner as described in the literature.

Copper Powder.—It was precipitated from an aqueous solution of cupric sulfate by addition of zinc granules and washed with water, dilute hydrochloric acid and finally with ethanol.

β-Naphthol.—Commercial reagent, m. p. 120~121°C (uncorr.).

p-Bromotoluene.—Commercial reagent was redistilled, m. p. 25.2°C.

Synthesis of α-Naphthyl *p*-Tolyl Ether.—*p*-Cresol was dissolved in an aqueous solution of potassium hydroxide and water was evaporated from the resulting solution in vacuo and to the dried residue were added α-bromonaphthalene and copper powder and the mixture was heated in an oil bath. The cooled mixture was first treated with 20% aqueous solution of potassium hydroxide to dissolve unreacted *p*-cresol and then extracted with benzene. The extract was concentrated and distilled in vacuo. The main fraction was at first pale yellow and viscous which gradually solidified to a white mass by cooling and seeding. This solid was recrystallized once from ethanol to give needles which melted at 36~39°C. The experimental results are shown in Table II.

The crude ether was recrystallized twice from ethanol to give colorless plates which melted at 38~39°C.

Found: C, 86.96; H, 5.71; mol. wt. 234. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02%; mol. wt. 234.

Solubility.—It is readily soluble in toluene, benzene, chloroform, moderately soluble in cold ethanol and insoluble in water.

Trinitrobenzene Complex.—It was prepared from ether (189 mg.) and trinitrobenzene (182 mg.) in ethanol. Three recrystallizations from ethanol yielded 192 mg. of pale yellow crystals, m. p. 72~73°C.

Found: N, 9.20. Calcd. for $C_{23}H_{17}O_7N_3$: N, 9.40%.

The picrate could not be prepared by the usual method.

Infrared Spectrum. — The spectrum in carbon disulfide is shown in Fig. 1. To make the analysis of the spectrum easier, a comparison with that of the α-phenyl ether is shown in Fig. 2. A band appearing at 13 μ (769 cm⁻¹) and 3 strong bands in the range of 9~10 μ correspond to a 1,2,3-substitution in the benzene ring. This means a substitution in 1-position of naphthalene which may be regarded as a substituted benzene. A band at

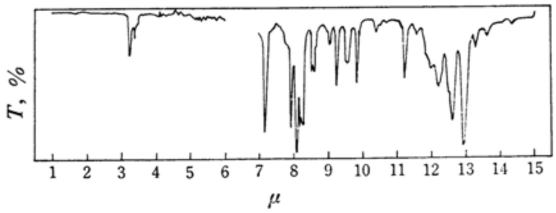

Fig. 1. α-Naphthyl *p*-tolyl ether.

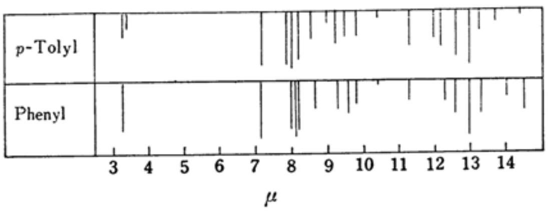

Fig. 2. Aryl α-naphthyl ether.

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[3] I. Heilbron, "Dictionary of Organic Compounds", Vol. 1, Oxford University Press, New York (1953), p. 613.

[4] "Organic Syntheses", Collective Vol. I, Second Edition, John Wiley & Sons, Inc., New York (1956), p. 121.

8.1 μ(1235 cm^{-1}) corresponds to an ether linkage and a band at 3.45 μ(2899 cm^{-1}) to aliphatic C-H. As a band at 12.2 μ(820 cm^{-1}) indicates the presence of a para-substitution in the benzene ring, the methyl group is at para position of the phenoxyl bonding. An absorption band at 12.6 μ(794 cm^{-1}) shows 3 adjacent hydrogen atoms in the benzene ring.

Synthesis of β-Naphthyl p-Tolyl Ether.—β-Naphthyl ether was synthesized in the same ways as those for α-napththyl ether. The experimental results are shown in Table III.

The crude ether (9.25 g.) was recrystallized from ethanol to give 3.17 g. of short needles, m. p. 41~42°C. This purified specimen distilled at 187~188°C (3 mmHg).

Found: C, 87.22; H, 6.00; mol. wt. 233. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02%; mol. wt. 234.

Solubility.—It is readily soluble in benzene, toluene and chloroform, moderately soluble in cold ethanol and insoluble in water.

Trinitrobenzene Complex.—It was prepared from the ether and trinitrobenzene in ethanol.—Recrystallized twice from ethanol, pale yellow leaflets were obtained; m. p. 93~94°C. This seems to be unstable.

Infrared Spectrum. — The spectrum in carbon disulfide is shown in Fig. 3 and the comparison with that of the β-phenyl ether is shown in Fig. 4. In this spectrum a band is absent at 14.5 μ. A strong band at 12.2 μ(820 cm^{-1}) shows a para-substitution in the benzene ring, thus indicating the presence of the methyl group at para position. A band at 13.4 μ(746 cm^{-1}) corresponds to the presence of 4 adjacent hydrogen atoms in the benzene ring.

Ultraviolet Spectra. — The spectra of α- and β-isomers of p-tolyl ethers and phenyl ethers in cyclohexane are shown in Figs. 5 and 6. Compared with the adsorption maxima of the corresponding phenyl ethers, those of p-tolyl ethers are at nearly the same wavelengths.

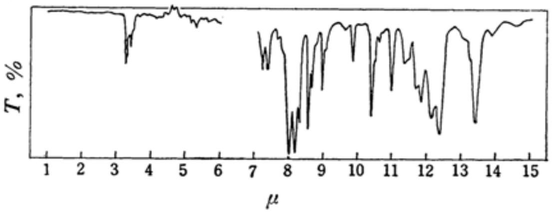

Fig. 3. β-Naphthyl p-tolyl ether.

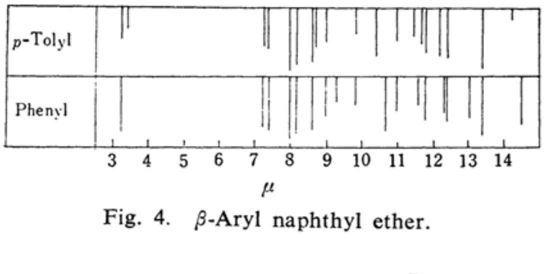

Fig. 4. β-Aryl naphthyl ether.

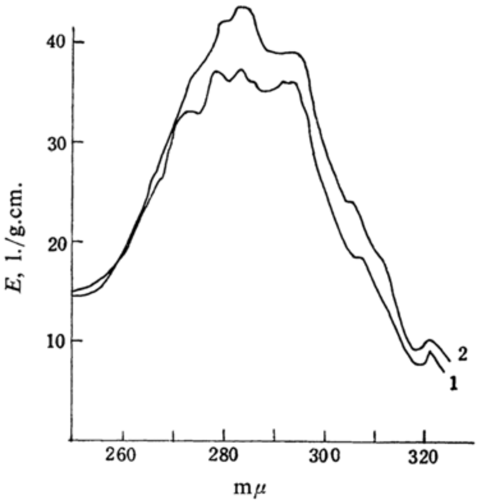

Fig. 5. α-Naphthyl ethers: 1, Phenyl; 2, p-Tolyl.

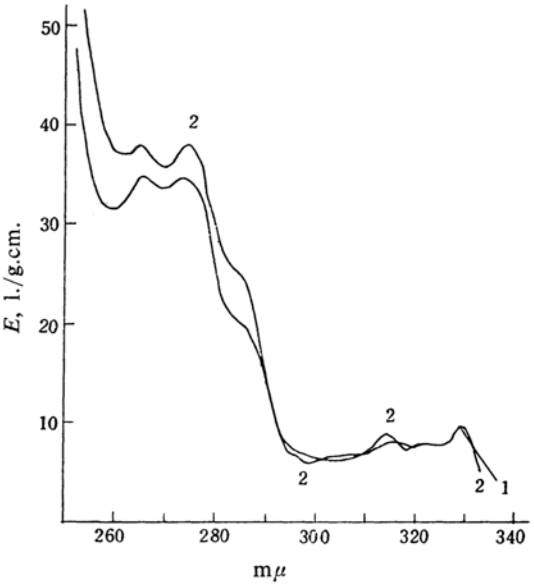

Fig. 6. β-Naphthyl ethers; 1, Phenyl; 2, p-Tolyl.

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