# *Synthesis of Phenanthryl Phenyl Ethers*

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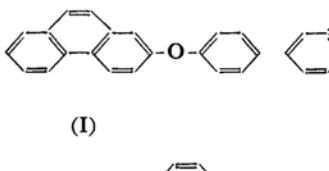
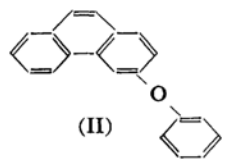
Searching for aromatic ethers which have high boiling points and thermal stability, derivatives of phenanthrene, 2- and 3-phenanthrylphenyl ethers (Formulas I and II respectively) were synthesized and their physical properties examined. Of the phenanthrylphenyl ethers, only a 9-phenyl isomer (Formule III) has hitherto been reported on the literature[1].



(I)



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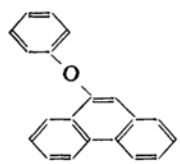
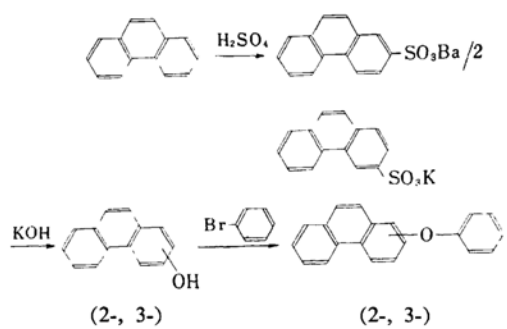


(III)

The author newly synthesized 2- and 3-phenyl ethers by the scheme shown below.

TABLE I




(2-, 3-) (2-, 3-)

1) R. L. Huang, *J. Chem. Soc.*, 1955, 3295.

Purified phenanthrene was sulfonated[2], and a mixture of monosulfonates was fused with potassium hydroxide[3], yielding phenanthrols which were then condensed with bromobenzene to give the ethers. The properties of purified specimens are shown in Table II.

TABLE II. PHENANTHRYLPHENYL ETHERS

| Properties | Isomer 2- | Isomer 3- | Calcd. |
|---|---|---|---|
| Appearence | White needles | White needles | — |
| B. p., °C | 225( 1mmHg) | 220 (1 mmHg) | — |
| M. p., °C | 121～122 | 86～87 | — |
| Elementary analysis | | | |
| C, % | 88.69 | 89.16 | 88.86 |
| H, % | 5.00 | 5.39 | 5.22 |
| Trinitrobenzene complex | | | |
| M. p., °C | 133～134 | 111～112 | — |
| Appearence | Pale yellow needles | Pale yellow leaflets | — |
| N, % | 8.91 | 8.96 | 8.70 |

## Experimental

**Materials.** — *Phenanthrene.* — A sample supplied by Yawata Chemical Industry Co. was purified by fusion with potassium hydroxide, followed by vacuum distillation, recrystallization from ethanol and treatment with chromium trioxide; m. p. 97～98.5°C, reported 98.7～99.5°C[4].

*Bromobenzene.* — A commercial reagent was redistilled; $n_D^{20.5}$ 1.5598, reported $n_D^{20}$ 1.5602[5].

2) "Org. Synth.", Col. Vol. II (1955), p. 482.
3) Fieser, *J. Am. Chem. Soc.*, 51, 2466 (1929).
4) J. Heilbron, "Dictionary of Org. Compds.", Vol. IV, Oxford University Press, New York (1953), p. 84.
5) Merck Index, 7th Edition, Merck & Co. Inc., Rahway, N. J. (1960), p. 168.

*Copper Powder.*—This was precipitated from an aqueous solution of $CuSO_4 \cdot 5H_2O$ by the addition of zinc granules and was washed with water, with dilute hydrochloric acid, and finally with ethanol.

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

**Synthesis of 2- and 3-Phenanthrol.** — Purified phenanthrene (50 g.)* was sulfonated by the method described in the literature[2]. From the reaction mixture, less soluble mono-sulfonic acids were separated as sodium salts, leaving disulfonates in the filtrate. By recrystallizing sodium mono-sulfonates from water, the relatively insoluble 2-isomer was first obtained, which was further purified as barium salt. From the filtrate, by concentration and the addition of potassium chloride, potassium 3-sulfonate was obtained. 2-Ba-sulfonate; 14.1 g., 16% (reported 17~21%). 3-K-sulfonate; 17.6 g., 21% (reported 24~26%). Then the sulfonates were fused with potassium hydroxide. To potassium hydroxide (about 3 parts) melted in a nickel crucible at 290~300°C, barium or potassium sulfonate (1 part) was added gradually over a period of 20 min. by stirring; the heating was continued for a further 5 min. at 320~330°C. The mixture was then allowed to cool and was dissolved in water. The addition of hydrochloric acid to this solution yielded a precipitate which was filtered off.

The precipitate was redissolved in an aqueous solution of potassium hydroxide and filtered off to remove insoluble matter. By the neutralization of the filtrate, crude phenanthrols were obtained which were filtered off and recrystallized from a mixture of ligroin and ethanol. The results of the potassium hydroxide fusion are shown in Table III.

TABLE III

| Phenanthrene sulfonate | Amount g. | Phenanthrol Amount g. | Phenanthrol M. p. °C | Reported m. p. °C |
|---|---|---|---|---|
| 2-Ba | 14 | 5.5 | 162.7~167.7<br>166~168 (purified) | 168 |
| 3-K | 17 | 10.3 | 112.6~118.5<br>116.8~118.9 (purified) | 118~119 |

**Synthesis of 2-Phenanthryl Phenyl Ether.** — A mixture of 2-phenanthrol, potassium hydroxide bromobenzene and copper powder in a flask fitted with an air condenser was placed in an oil bath and heated. The cooled mixture was first treated with a 10% aqueous solution of potassium hydroxide to dissolve unreacted phenanthrol and was then extracted repeatedly with benzene. The combined extracts were concentrated and distilled in vacuo. The distillation apparatus employed was designed for distilling solid samples and equipped with a fractionating column (10 mm.×350 mm.) packed with stainless Dixon packing 2 mm. in diameter. The distillate, which was solid melting at about 110~116°C, was recrystallized 3 times from ethanol, yielding white needles. The experimental results of the condensation reaction are shown in Table IV.

* One tenth of the amount used in Ref. 2.

Found: C, 88.69; H, 5.00; mol. wt. (Rast), 273. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22%; mol. wt. 270.

*Infrared Absorption Spectrum.*—The spectrum of 2-phenanthryl phenyl ether in carbon bisulfide is shown in Fig. 1. The band appearing at 825 $cm^{-1}$

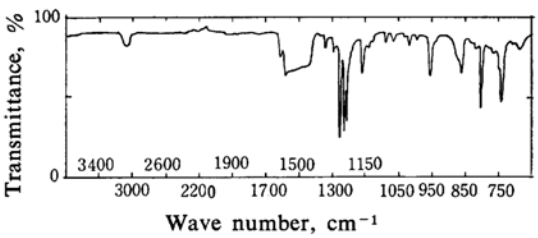



Fig. 1. 2-Phenanthryl phenyl ether.

corresponds to a 1,2,4-substitution in the benzene ring. This means a substitution in the 2- or 3-position of phenanthrene, which may be regarded as a substituted benzene. Similarly, because an absorption band at 807 $cm^{-1}$ which corresponds to a 1,2,3,4-substitution in benzene is absent, the 9- or 10-position of phenanthrene is not substituted. The absence of a strong absorption in the region of 752~753 $cm^{-1}$ shows that a 1,2,3-substitution in the benzene ring is not present; that is, there is no substitution in the 1- or 4-position of phenanthrene. The spectrum which shows characteristic absorptions of 2- or 3-substituted phenanthrene can be clearly distinguished from that of a 3-phenyl isomer, which will be described later. A band at 690 $cm^{-1}$ may be assigned to a phenoxy group. Phenoxynaphthalenes ($\alpha$, $\beta$), *p*-phenoxydiphenyl, and *p,p'*-diphenoxydiphenyl which the author prepared showed a medium absorption in the vicinity of this wave number.

*Ultraviolet Spectra.*—The spectra of the 2-phenyl as well as the 3-phenyl isomer are shown in Fig. 2.

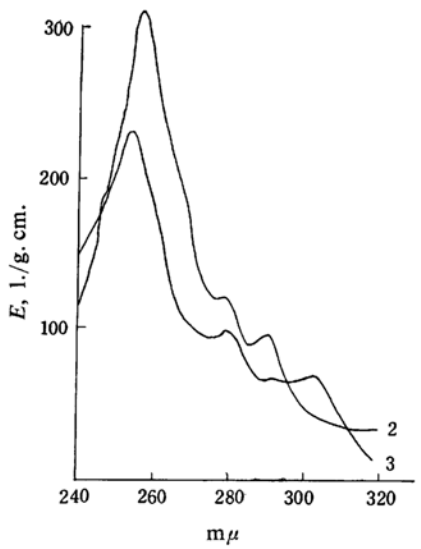



Fig. 2

2, 2-Phenyl isomer; 3, 3-Phenyl isomer

TABLE IV. 2-PHENANTHRYL PHENYL ETHER

| No. | 2-Phenanthrol[a] g. | Bromobenzene g. | KOH g. | Cu g. | Condition Temp. °C | Condition Time hr. | Distillate g. | Recrystallized Amount g. | Recrystallized M. p. °C | Recrystallized Yield[b] % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.2 | 3.1 | 1.3 | 0.2 | 150~200 | 2 1/3 | 3.1 | 1.6 | 120~121 | 27 |
| 2 | 1.1 | 2.0 | 0.35 | 0.05 | 170~185 | 3 5/6 | 0.89 | 0.45 | 120~121 | 29 |
| 3 | 4.2 | 5.9 | 1.3 | 0.2 | 140~200 | 5 | 4.5 | 2.50 | 121~122 | 43 |

a) M. p. of phenanthrol; Nos. 1 and 2, 162.7~167.7°C; No. 3, 166~168°C.
b) Mol. % based on 2-phenanthrol employed.

TABLE V. 3-PHENANTHRYL PHENYL ETHER

| No. | 3-Phenanthrol[a] g. | Bromobenzene g. | KOH g. | Cu g. | Condition Temp. °C | Condition Time hr. | Distillate g. | Recrystallized Amount g. | Recrystallized M. p. °C | Recrystallized Yield[b] % |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5.5 | 4.0 | 1.7 | 0.20 | 150~200 | 5 1/2 | 5.3 | 2.35 | 85~86 | 31 |
| 2 | 3.1 | 5.4 | 1.0 | 0.13 | 160~170 | 4 1/2 | 1.99 | 1.32 | 86~87 | 31 |
| 3 | 4.2 | 5.9 | 1.3 | 0.20 | 140~200 | 5 | 4.8 | 2.95 | 86~87 | 50 |

a) M. p. of 3-phenanthrol; Nos. 1 and 2, 112.6~118.5°C; No. 3, 116.8~118.9°C.
b) Mol. % based on 3-phenanthrol employed.

The absorption maxima are different from those of 2- or 3-alkyl phenanthrene.

*Solubility.*—It is only with difficulty soluble in cold ethanol, readily soluble in benzene, and insoluble in water.

*Trinitrobenzene Complex.*—This was prepared from 2-phenanthryl phenyl ether (86 mg.) and 72 mg. of trinitrobenzene in ethanol. Three recrystallizations from ethanol yielded 45 mg. of short yellow needles, which melted at 133~134°C.

Found: N, 8.91, Calcd. for $C_{26}H_{17}O_7N_3$; N, 8.70%.

**Synthesis of 3-Phenanthryl Phenyl Ether.**—The 3-phenyl isomer was prepared and purified in the same manner as in the case of the 2-phenyl isomer. The experimental results are shown in Table V.

Recrystallization from ethanol gave white needles which melted at 86~87°C.

Found: C, 89.16; H, 5.39; mol. wt. (Rast), 273. Calcd. for $C_{20}H_{14}O$: C, 88.86; H, 5.22%; mol. wt., 270.

*Infrared Spectrum.*—The spectrum in carbon disulfide is shown in Fig. 3.

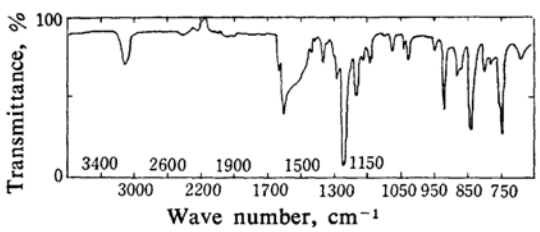



Fig. 3. 3-Phenanthryl phenyl ether.

A band at 690 $cm^{-1}$ corresponds to a phenoxyl group. Other absorption bands appearing in the finger print region are typical of 3-substituted phenanthrene, as a comparison with those of 3-ethylphenanthrene[6] shows:

| | Wave numbers, $cm^{-1}$ | | | | |
|---|---|---|---|---|---|
| 3-Phenanthryl phenyl ether | 880 | 865 | 840 | 798 | 747 |
| 3-Ethylphenanthrene | 881 | 864 | 839 | 800 | 746 |

*Ultraviolet Spectrum.*—The spectrum is shown in Fig. 2.

*Solubility.*—It is only with difficulty soluble in cold ethanol, moderately soluble in benzene, and insoluble in water.

*Trinitrobenzene Complex.*—This was prepared from ether (99 mg.) and trinitrobenzene (108 mg.) in ethanol. Three recrystallizations from ethanol yielded 73 mg. of a pale yellow adduct, m. p. 111~112°C.

Found: N, 8.96. Calcd. for $C_{26}H_{20}O_7N_3$, N, 8.70%.

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6) E. Ochiai, et al., *Pharm. Bull.*, **5**, 113 (1957).