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Hard Acid and Soft Nucleophile System. VI.[1] A Convenient Synthesis of Alkylthiopolycyclic Aromatics with a Metal Halide and Thiol System

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On treatment with a metal halide and alkanethiol system, polycyclic aromatics having various substituents such as hydroxy, alkoxy, phenoxy, acetoxy, and halogen were easily converted into alkylthiopolycyclic aromatics in high yields. The chemo and regioselectivity are described for the reaction of disubstituted naphthalenes.

Keywords——hard acid; soft nucleophile; aromatic sulfide; aluminum chloride; naphthalene; phenanthrene; anthracene; MO calculation

We have reported that the combination system of a hard acid and a soft nucleophile effectively cleaves a variety of carbon-oxygen bonds.[2] In the course of our investigation on the dealkylation of alkyl ethers of phenols with this system, it was found that the alkoxy group of polycyclic aromatics was defunctionalized to afford the corresponding parent aromatics *via* the sulfide as a reaction intermediate.[3] It might be possible, therefore, to use the combination system for the synthesis of alkylthiopolycyclic aromatics. This paper deals with experimental confirmation of the idea described above.

The known synthetic procedures[4] for aklylthiopolycyclic aromatics can be divided into two main classes on the basis of the reaction type, namely, alkylation of the corresponding thiols[5] and substitution of functional groups (*e.g.* OH,[6] Br,[7] or NO_2[8]) with alkanethiols. Although the former is considered to be the best method, it is disadvantageous as regards substrate availability. The latter has at least one shortcoming from the viewpoint of the yield, the reaction conditions, or the generality. These difficulties have been overcome by the present method, which is schematically presented in Chart 1.

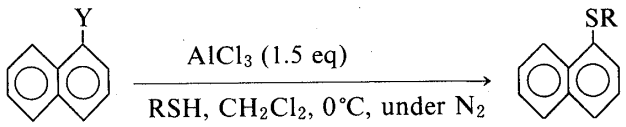
$$\text{Ar-Y} + \text{RSH} \xrightarrow{\text{metal halide}} \text{Ar-SR}$$

Ar: Polycyclic aromatics
Y: *O*-alkyl, *O*-aryl, *O*-acyl, halogen

Chart 1

The reaction of α-methoxynaphthalene with various thiols was investigated first, and the results are listed in Table I. The best result was obtained with 1.5 molar equivalent of aluminum chloride as a Lewis acid at 0°C. A longer reaction time and a larger amount (*ca.* 2.5 mol eq) of aluminum chloride at room temperature accelerated the reduction of the resulting sulfide to give naphthalene.[3] In the case of benzene thiol the lower nucleophilicity of the sulfur atom considerably reduces the rate of formation of α-naphthyl phenyl sulfide to a level comparable with that of the subsequent reduction of the sulfide, which makes it impossible to isolate the sulfide (entry 5 in Table I). However, β-naphthyl phenyl sulfide was obtained from the corresponding methoxynaphthalene under the same reaction conditions (entry 5 in Table II) because it was rather stable to the reagent system used.[9]

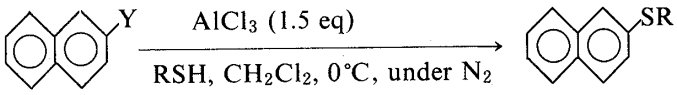
TABLE I. Preparation of α-Naphthyl Alkyl (Aryl) Sulfides



Entry	Substrate Y (mmol)	Thiol R (ml)	CH_2Cl_2 (ml)	Time	Yield[a] (%)
1	OMe (1.0)	Et (0.4)	2.0	40 min	92.0
2	OMe (5.6)	iso-Bu (2.6)	10.0	5.5 h	98.3
3	OMe (5.0)	*n*-Oct (3.7)	10.0	2.0 h	90.9
4	OMe (6.0)	iso-Pr (2.4)	10.0	5.5 h	92.1
5	OMe 4.9)	Ph (2.0)	10.0	27.0 h[b]	0[c]
6	OEt (3.0)	Et (1.0)	5.0	1.0 h	84.8
7	OPh (1.0)	Et (0.4)	2.0	40 min	92.0
8	OH (1.0)	Et (0.4)	2.0	1.0 h	86.2
9	OAc (3.0)	Et (1.0)	5.0	16.0 h	61.2
10	F (3.0)	Et (1.0)	5.0	1.0 h	79.2
11	Br (3.0)	Et (1.0)	5.0	8.0 h	66.8

a) Isolated yield.
b) The reaction was carried out at room temperature.
c) Naphthalene was obtained in 71.1% yield.

TABLE II. Preparation of β-Naphthyl Alkyl (Aryl) Sulfides



Entry	Substrate Y (mmol)	Thiol R (ml)	CH_2Cl_2 (ml)	Time	Yield[a] (%)
1	OMe (1.0)	Et (0.4)	2.0	50 min	96.8
2	OMe (5.8)	iso-Bu (2.6)	10.0	1.2 h	98.6
3	OMe (5.0)	*n*-Oct (3.7)	10.0	1.5 h	91.3
4	OMe (6.0)	iso-Pr (2.4)	10.0	8.0 h	93.5
5	OMe (3.0)	Ph (1.3)	6.0	27.5 h[b]	81.3
6	OEt (1.0)	Et (0.4)	2.0	25 min	93.6
7	OPh (1.0)	Et (0.4)	2.0	1.5 h	95.6
8	OH (1.0)	Et (0.4)	2.0	20 min	93.4
9	OAc (1.0)	Et (0.4)	2.0	14.0 h[b]	87.2
10	OCOPh (1.0)	Et (0.4)	2.0	5.0 d[c]	65.1
11	Cl (0.9)	Et (0.3)	1.5	8.5 h	80.1
12	Br (3.0)	Et (1.0)	5.0	10.0 h	84.8

a) Isolated yield.
b) The reaction was carried out at room temperature.
c) The reaction was carried out with 2.5 mol equivalents of $AlCl_3$ at room temperature.

A possible mechanism of the sulfide formation from α-methoxynaphthalene is shown in Chart 2. Thus, the coordination of aluminum chloride with α-methoxynaphthalene at C-4 gives an intermediate species **a** followed by the attack of a thiol on the *ipso*-carbon to afford **b**. The order of the reactivity of thiols (primary>secondary≧aromatic) indicates that this step should be rate determining. The subsequent elimination of the methoxy group gives rise to the α-naphthyl sulfide. Exactly the same type of mechanism except for the position of the initial attack of aluminum chloride should be operative in the case of β-methoxynaphthalene. The molecular orbital calculation for methoxynaphthalenes by CNDO/2[10] revealed a close relationship between the position of the initial attack of aluminum chloride and the coefficient of the highest occupied molecular orbital (HOMO). Thus, the atom with the largest coefficient in the HOMO (C-4 and C-1 in α- and β-methoxynaphthalenes, respectively) was attacked by

TABLE III. Preparation of 9-Ethylthiophenanthrene and 9-Ethylthioanthracene

$$\text{Ar-Y} \xrightarrow[\text{EtSH, } CH_2Cl_2, N_2]{\text{Metal Halide}} \text{Ar-SEt}$$

Entry	Substrate Ar	Substrate Y(mmol)	Metal halide (molar eq.)	EtSH (ml)	CH_2Cl_2 (ml)	Temp. (°C)	Time	Product (yield, %)[a]
1	Phenanthryl	9-OEt (1.0)	$AlCl_3$(2.5)	0.4	2	r.t.	2.5 h	A[b] (0)[c]
2	Phenanthryl	9-OEt (0.5)	$AlCl_3$ (1.5)	0.2	1	0	10 min	A (92.5)
3	Phenanthryl	9-OEt (0.5)	$ZnCl_2$ (2.6)	0.2	1	r.t.	20.0 h	A (93.3)
4	Phenanthryl	9-OEt (0.5)	$ZnBr_2$ (2.5)	0.2	1	r.t.	5.0 h	A (99.8)
5	Phenanthryl	9-OEt (0.5)	$TiCl_4$ (2.7)	0.2	1	r.t.	3.0 h	A (98.7)
6	Phenanthryl	9-OEt (0.5)	$FeCl_3$ (2.6)	0.2	1	r.t.	3.0 h	A (97.5)
7	Phenanthryl	9-OEt (0.5)	$SbCl_5$ (1.5)	0.2	1	r.t.	3.5 h	A (31.0)
8	Phenanthryl	9-OH (1.0)	$ZnCl_2$ (1.6)	0.4	2	0	4.0 h	A (69.2)
9	Phenanthryl	9-Br (1.0)	$AlCl_3$ (1.7)	0.4	2	0	10 min	A (84.7)
10	Anthryl	9-OEt (0.4)	$AlCl_3$ (2.6)	0.2	1	0	30 min	B[d] (0)[e]
11	Anthryl	9-OEt (1.0)	$ZnCl_2$ (1.5)	0.4	2	0	40 min	B (98.3)
12	Anthryl	9-Br (3.0)	$ZnCl_2$ (1.5)	1.0	5	0	2.0 h	B (47.1)

a) Isolated yield.
b) A=9-Ethylthiophenanthrene.
c) Phenanthrene was obtained in 95.5% yield.
d) B=9-Ethylthioanthracene.
e) Anthracene was obtained in 84.5% yield.

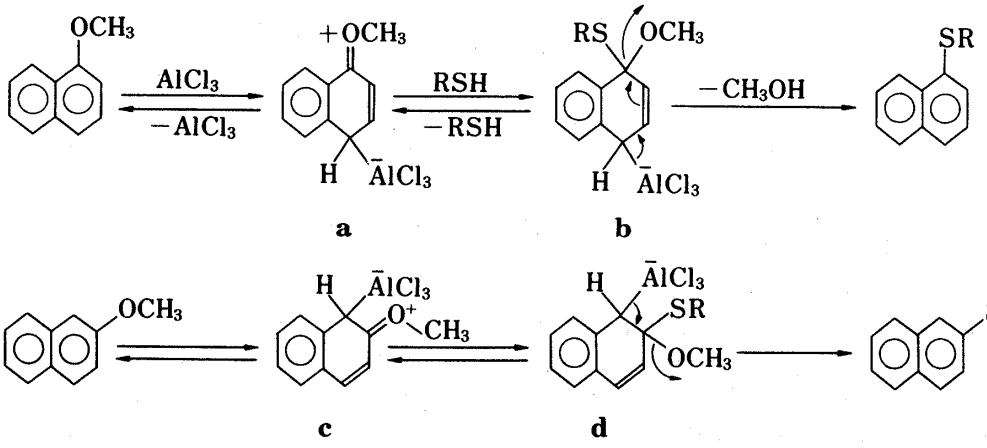


Chart 2

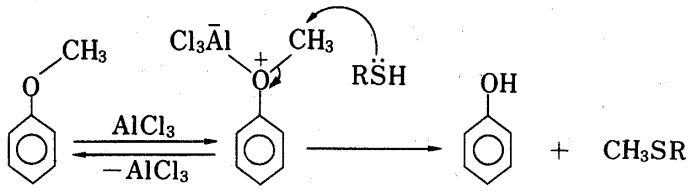


Chart 3

aluminum chloride at the initial stage of the reaction. It is interesting to note that the HOMO of anisole has the largest coefficient on the oxygen atom, in accord with the facile demethylation of this molecule under the same reaction conditions, as shown in Chart 3.[2d,e]

Hydroxy, ethoxy, phenoxy, benzoyloxy, acetoxy and halogen were effectively replaced by an ethylthio group under nearly the same conditions. The rate of formation of the sulfide

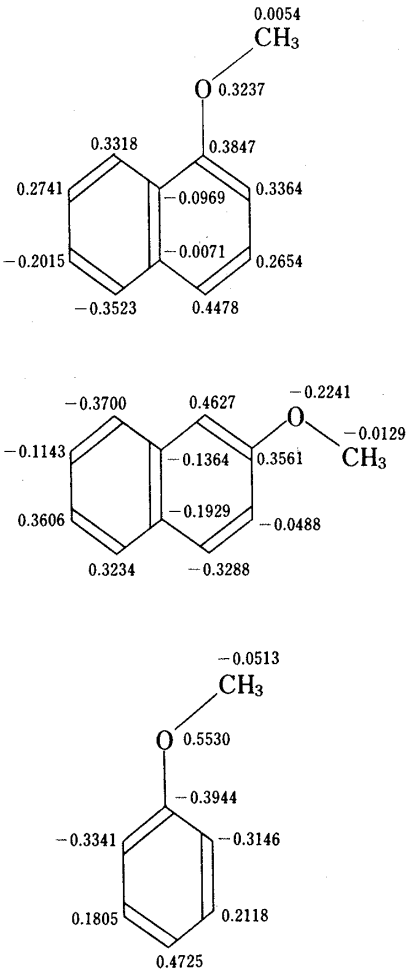


Fig. 1. Coefficients of the HOMO in α- and β-Methoxynaphthalene and Anisole

decreases in the order of ether, hydroxy, halogen and ester. The tendency that shorter reaction times gave a higher yield of the product than longer times should be attributable to the further reduction of the sulfide formed.

The derivatives of polycyclic aromatics such as anthracene and phenanthrene showed extremely high reactivity under the same conditions to give the corresponding sulfides (Table III). All metal halides tested, except antimony pentachloride, converted 9-ethoxyphenanthrene into the corresponding sulfide in nearly quantitative yield (entries 2—6). 9-Bromophenanthrene was converted into the corresponding sulfide with aluminum chloride at 0°C in 10 min (entry 9). Other metal halides formed an insoluble precipitate with bromophenanthrene and the desired sulfide was not obtained. 9-Substituted anthracenes were the most reactive substrate for a metal halide and ethanethiol system. Anthracene was obtained from 9-ethoxyanthracene with aluminum chloride within 30 min (entry 10). On the other hand, 9-ethylthioanthracene was obtained in high yield when zinc chloride, which was considered as the mildest halide tested, was used (entry 11). The reactivity of zinc chloride was not sufficient to convert 9-bromoanthracene into the corresponding sulfide in good yield (entry 12). From the results mentioned above it is desirable to select alkoxy derivatives as a starting material for the preparation of polycyclic aromatic sulfides.

2-Bromo-6-ethoxynaphthalene (**1**) gave an inseparable mixture of 2-bromo-6-ethylthionaphthalene (**4**) and 2-ethylthionaphthalene under the normal reaction conditions with dichloromethane as a cosolvent. The formation of 2-ethylthionaphthalene may involve the one-electron oxidation[3] of the product, bromosulfide **4**, because aluminum chloride has been proved to be an effective one-lectron oxidant when it is used in dichloromethane.[11] The absence of dichloromethane in the reaction mixture resulted in the chemoselective formation of 2-bromo-6-ethylthionaphthalene (**4**) in good yield, as expected from the results with of β-bromo and β-ethoxynaphthalenes. 1,6-Diethoxynaphthalene (**2**) afforded the corresponding sulfide **5** without dichloromethane as a cosolvent, but otherwise gave a low yield of **5** because of the subsequent reaction initiated by aluminum chloride. 1,3-Dihydroxynaphthalene (**3**) gave the sulfide **6** as a sole product in high yield. Characteristic proton magnetic resonance (^{1}H-NMR) signals of protons at C-2 (δ 6.72, d, J=1.7 Hz) and at C-8 (δ 8.09, m) excluded an alternative structure **7**. The observed regioselective formation of **6** might be governed by the relative stability of the intermediate species **e** and **f** leading to **6** and **7**, respectively. Conjugation of the double bond

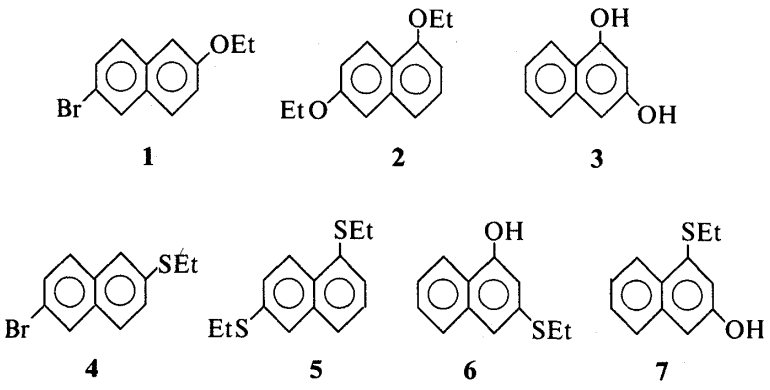
e **f**

Chart 4

TABLE IV. The Reaction[a] of Disubstituted Naphthalenes

Substrate (mmol)	$AlCl_3$ (mol eq)	EtSH (ml)	CH_2Cl_2 (ml)	Time (h)	Temp.	Product (yield, %)[b]
1(0.5)	1.5	1	—	1	0°C	**4**(73.5)
2(0.6)	5.6	2	—	1	r.t.	**5**(82.5)
3(1.0)	3.0	0.4	2	0.5	r.t.	**6**(96.6)

a) All reactions were carried out under a nitrogen atmosphere.
b) Isolated yield.



with the adjacent aromatic ring in **e** should lower the free energy of this intermediate species compared with that of **f** having an isolated double bond.

In summary, we have shown that the metal halide and thiol system is extremely useful for the preparation of alkyl polycyclic aromatic sulfides. The remarkable feature of this reagent system is the specificity for the polycyclic aromatics. The simple aromatics (benzene derivatives) did not afford the corresponding sulfide but reacted in a different fashion or remained intact under the same reaction conditions. It is noteworthy that various oxygenated substituents and halogens can serve as a starting functionality. The advantages of the present method include high yield, mild reaction conditions, short reaction time, and simple work-up procedure.

Experimental

Melting points were taken with a micro hot-stage apparatus (Yanagimoto) and they are uncorrected. Boiling points were determined on a micro distillation apparatus. The infrared (IR) spectra were recorded with a JASCO A-202 diffraction grating infrared spectrophotometer and ^{1}H-NMR spectra were obtained with a JEOL JNM-FX-100 spectrometer or JEOL JNM-PMX 60 spectrometers with tetramethylsilane as an internal standard. Mass spectra (MS) were determined on a JEOL JMS-01SG mass spectrometer. A Büchi GKR-50 apparatus was used for Kugelrohr distillation. Kieselgel 60 (0.063—0.2 mm Merck) was used for column chromatography, and Kieselgel 60 F254 plates for thin layer chromatography (TLC) and preparative TLC.

Materials——α-Phenoxynaphthalene and β-phenoxynaphthalene were prepared by use of the Ullmann reaction.[12] 9-Ethoxyphenanthrene and 9-ethoxyanthracene were prepared by the method of Bacon.[13] 2-Naphthyl benzoate was prepared from 2-naphthol and benzoyl chloride. 2-Bromo-6-ethoxynaphthalene (**1**) and 1,6-diethoxynaphthalene were prepared by usual treatment of 2-bromo-6-naphthol and 1,6-dihydroxynaphthalene, respectively, with diethyl sulfate and potassium carbonate.

Other materials were commercial products.

2-Naphthyl benzoate——Colorless needles; mp 106—109°C (from petroleum ether–dichloromethane). NMR ($CDCl_3$) δ: 7.29—7.93 (10H, m), 8.20—8.30 (2H, m). *Anal.* Calcd for $C_{17}H_{18}O_2$: C, 82.24; H, 4.87. Found: C, 81.97; H, 4.89.

2-Bromo-6-ethoxynaphthalene (1)——Colorless plates; mp 82—83°C (from petroleum ether–dichloromethane). NMR ($CDCl_3$) δ: 1.48 (3H, t, J=6.7 Hz), 4.14 (2H, q, J=6.7 Hz), 7.10—7.90 (6H, m). *Anal.* Calcd for $C_{12}H_{11}BrO$: C, 57.39; H, 4.42. Found: C, 57.17; H, 4.26. MS m/e: 250 (M^+).

1,6-Diethoxynaphthalene (2)———Colorless needles; mp 87—89°C (from petroleum ether–dichloromethane). NMR ($CDCl_3$) δ: 1.47 (3H, t, J=7.2 Hz), 1.52 (3H, t, J=7.1 Hz), 4.14 (2H, q, J=7.2 Hz), 4.18 (2 H, q, J=7.1 Hz), 6.67 (1H, m), 7.06—7.33 (4H, m), 8.18 (1H, d, J=9.8 Hz). *Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.46; H, 7.41. MS m/e; 216 (M^+).

General Procedure for Preparation of Sulfides———The substrate was added to a stirred solution of a metal halide in a thiol and dichloromethane (purified by distillation from CaH_2) under the conditions described in Tables I—IV.

The reaction was monitored by TLC after the metal halide had been quenched with methanol in the capillary. The reaction mixture was poured into water, then dilute hydrochloric acid was added, and the mixture was extracted with dichloromethane. The organic layer was shaken with brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated to leave a crude material, which was purified by chromatography over a silica gel column. The product was purified by recrystallization or distillation to give analytical samples.

Ethyl α-Naphthyl Sulfide———Colorless oil; bp 110—111°C (1.0 mmHg). IR $\nu_{max}^{CHCl_3}cm^{-1}$: 1590, 1560, 1505, 1445, 1420, 1380. NMR ($CDCl_3$) δ: 1.32 (3H, t, J=7.3 Hz), 3.00 (2H, q, J=7.3 Hz), 7.40—7.86 (6H, m), 8.28—8.42 (1H, m). *Anal.* Calcd for $C_{12}H_{12}S$: C, 76.54; H, 6.42. Found: C, 76.91; H, 6.49.

Isobutyl α-Naphthyl Sulfide———Colorless oil; bp 107—108°C (0.15 mmHg). IR $\nu_{max}^{CHCl_3}cm^{-1}$: 1595, 1505, 1460, 1380. NMR ($CDCl_3$) δ: 1.01 (6H, d, J=6.6 Hz), 1.86 (1H, nonet, J=6.6 Hz), 2.82 (2H, d, J=6.6 Hz), 7.32—7.81 (6H, m), 8.37—8.46 (1H, m). *Anal.* Calcd for $C_{14}H_{16}S$: C, 77.72; H, 7.46. Found: C, 77.63; H, 7.69.

α-Naphthyl *n*-Octyl Sulfide———Colorless oil; bp 160°C (0.2 mmHg), NMR ($CDCl_3$) δ: 0.84 (3H, t, J=4.5 Hz), 0.6—2.0 (12H, m), 2.93 (2H, t, J=7.1 Hz), 7.25—7.83 (6H, m), 8.35—8.44 (1H, m). *Anal.* Calcd for $C_{18}H_{24}S$: C, 79.35; H, 8.88. Found: C, 79.35; H, 8.96. MS m/e: 272 (M^+).

Isopropyl α-Naphthyl Sulfide———Colorless oil; bp 112—113°C (1.0 mmHg). IR $\nu_{max}^{CHCl_3}cm^{-1}$: 1580, 1560, 1505, 1380, 1365. NMR ($CDCl_3$) δ: 1.27 (6H, d, J=6.6 Hz), 3.38 (1H, septet, J=6.6 Hz), 7.36—7.84 (6H, m), 8.47—8.56 (1H, m). *Anal.* Calcd for $C_{13}H_{14}S$: C, 77.17; H, 6.98. Found: C, 77.67; H, 7.12.

Ethyl β-Naphthyl Sulfide———Colorless oil; bp 119—120°C (0.2 mmHg). IR $\nu_{max}^{CHCl_3}cm^{-1}$: 1620, 1590, 1505, 1445, 1420, 1380. NMR ($CDCl_3$) δ: 1.33 (3H, t, J=7.3 Hz), 3.00 (2H, q, J=7.3 Hz), 7.33—7.52 (3H, m), 7.67—7.79 (4H, m). *Anal.* Calcd for $C_{12}H_{12}S$: C, 76.54; H, 6.42. Found: C, 76.88; H, 6.50.

Isobutyl β-Naphthyl Sulfide———Colorless oil; bp 126—127°C (0.7 mmHg). IR $\nu_{max}^{CHCl_3}cm^{-1}$: 1620, 1595, 1505, 1460, 1380, 1365. NMR ($CDCl_3$) δ: 1.04 (6H, d, J=6.6 Hz), 1.91 (1H, nonet, J=6.6 Hz), 2.88 (2H, d, J=6.6 Hz), 7.29—7.49 (3H, m), and 7.65—7.78 (4H, m). *Anal.* Calcd for $C_{14}H_{16}S$: C, 77.72; H, 7.46. Found: C, 77.74; H, 7.63.

β-Naphthyl *n*-Octyl Sulfide———Colorless crystals; mp 30—31°C (by distillation). IR $\nu_{max}^{CHCl_3}cm^{-1}$: 3060, 3020, 2920, 2850, 1610, 1586, 1504, 1454. NMR ($CDCl_3$) δ: 0.85 (3H, t, J=4.8 Hz), 0.6—2.0 (12H, m), 2.95 (2H, t, J=7 Hz), 7.1—7.9 (7H, m). *Anal.* Calcd for $C_{18}H_{24}S$: C, 79.35; H, 8.88. Found: C, 79.10; H, 9.15.

Isopropeyl β-Naphthyl Sulfide———Colorless oil; bp 120—121°C (2.5 mmHg). IR $\nu_{max}^{CHCl_3}cm^{-1}$: 1620, 1590, 1505, 1460, 1450, 1380, 1360. NMR ($CDCl_3$) δ: 1.31 (6H, d, J=6.6 Hz), 3.47 (1H, septet, J=6.6 Hz), 7.36—7.49 (3H, m), 7.67—7.82 (4H, m). *Anal.* Calcd for $C_{13}H_{14}S$: C, 77.17; H, 6.98. Found: C, 77.37; H, 7.10.

β-Naphthyl Phenyl Sulfide———Colorless needles; mp 51—52°C (from wet acetonitrile). IR $\nu_{max}^{CHCl_3}cm^{-1}$: 3060, 3025, 1610, 1580, 1503, 1425. NMR ($CDCl_3$) δ: 7.12—7.42 (8H, m), 7.58—7.78 (4 H, m). *Anal.* Calcd for $C_{16}H_{12}S$: C, 81.31; H, 5.12. Found: C, 81.33; H, 5.09.

Ethyl 9-Phenanthryl Sulfide———Colorless needles; mp 79—82°C (from petroleum ether–dichloromethane). NMR ($CDCl_3$) δ: 1.36 (3H, t, J=7.3 Hz), 3.04 (2H, q, J=7.3 Hz), 7.51—7.83 (6H, m), 8.42—8.71 (3H, m). *Anal.* Calcd for $C_{12}H_{14}S$: C, 80.62; H, 5.92. Found: C, 80.39; H, 5.96.

9-Anthryl Ethyl Sulfide———Yellow oil; IR $\nu_{max}^{CHCl_3}cm^{-1}$: 3020, 2970, 1437, 890. NMR ($CDCl_3$) δ: 1.1 (3H, t, J=7.5 Hz), 2.8 (2H, q, J=7.5 Hz), 7.3—7.6 (4H, m), 7.8—8.0 (2H, m), 8.3 (1H, br s), 8.5—9.0 (2H, m). High resolution MS Calcd for $C_{16}H_{14}S$: 238.074. Found: 238.078.

2-Bromo-6-ethylthionaphthalene (4)———Colorless crystals; mp 50—51°C (from MeOH). NMR ($CDCl_3$) δ: 1.34 (3H, t, J=7.3 Hz), 3.02 (2H, q, J= 7.3 Hz), 7.23—7.90 (6H, m). *Anal.* Calcd for $C_{12}H_{11}BrS$: C, 53.94; H, 4.15. Found: C, 53.81; H, 4.03. MS m/e: 266 (M^+).

1,6-Diethylthionaphthalene (5)———Colorless oil; bp 160°C (0.05 mmHg). NMR ($CDCl_3$) δ: 1.27, 1.32 (each 3H, t, J=7.3 Hz), 2.92, 2.99 (each 2H, q, J=7.3 Hz), 7.31—7.68 (5H, m), 8.27 (1H, dd, J=8.3, 0.7 Hz). *Anal.* Calcd for $C_{14}H_{16}S_2$: C, 67.69; H, 6.49. Found: C, 67.85; H, 6.60. MS m/e: 248 (M^+).

1-Hydroxy-3-ethylthionaphthalene (6)———Yellow oil; IR $\nu_{max}^{CHCl_3}cm^{-1}$: 3590, 3300, 1620, 1583, 1385, 1150. NMR ($CDCl_3$) δ: 1.27 (3H, t, J=7.0 Hz), 2.91 (2H, q, J=7 Hz), 5.99 (1H, br s, -OH), 6.72 (1H, d, J=1.7 Hz), 7.31—7.70 (4H, m), 8.09 (1H, m). High resolution MS Calcd for $C_{12}H_{12}OS$: M 204.061. Found: M^+ 204.060.

Calculations———Molecular orbital calculations by CNDO/2 were carried out with QCPE program No. 91 on a HITAC 8800/8700 computer at the Computation Center of Tokyo University. The geometries of the molecules (α- and β-methoxynaphthalene and anisole) were taken from the Cambridge Crystallographic Data File (CCDF).

References and Notes

1) Part V: M. Node, K. Nishide, M. Ochiai, K. Fuji and E. Fujita, *J. Org. Chem.*, **46**, 5163 (1981).
2) *a*) M. Node, H. Hori and E. Fujita, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 2237; *b*) M. Node, K. Nishide, M. Sai and E. Fujita, *Tetrahedron Lett.*, **1978**, 5211; *c*) K. Fuji, K. Ichikawa, M. Node and E. Fujita, *J. Org. Chem.*, **44**, 1661 (1979); *d*) M. Node, K. Nishide, M. Sai, K. Ichikawa, K. Fuji and E. Fujita, *Chem. Lett.*, **1979**, 97; *e*) M. Node, K. Nishide, K. Fuji and E. Fujita, *J. Org. Chem.*, **45**, 4275 (1980); *f*) K. Fuji, T. Kawabata and E. Fujita, *Chem. Parm. Bull.*, **28** , 3662 (1980); *g*) K. Fuji, T. Kawabata, M. Node and E. Fujita, *Tetrahedron Lett.*, **22**, 875 (1981); *h*) M. Node, K. Nishide, M. Sai, K. Fuji and E. Fujita, *J. Org. Chem.*, **46**, 1991 (1981); *i*) M. Ochiai, K. Nishide, M. Node and E. Fujita, *Chem. Lett.*, **1981**, 283.
3) M. Node, K. Nishide, K. Ohta and E. Fujita, *Tetrahedron Lett.*, **23**, 689 (1982).
4) For a recent review, see: S. Kozuka, *Yuki Goseikagaku Kyokaishi*, **39**, 825 (1981).
5) E. Vowinkel, *Synthesis*, **1974**, 430.
6) F.M. Furman, J.H. Thelin, D.W. Hein and W.B. Hardy, *J. Am. Chem. Soc.*, **82**, 1450 (1960).
7) R. Adams and A. Ferretti, *J. Am. Chem. Soc.*, **81**, 4927 (1959).
8) Y. Takikawa, T. Abe, R. Sato and S. Takizawa, *Chem. Lett.*, **1980**,25.
9) The difference of stability between α- and β-naphthyl phenyl sulfide under these reaction conditions will be discussed elsewhere.
10) J.A. Pople, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, 1970.
11) H. Bock and W. Kaim, *J. Am. Chem. Soc.*, **102**, 4429 (1980), and references cited therein.
12) F. Ullmann and P. Sponagel, *Justus Liebigs Ann. Chem.*, **350**, 83 (1906).
13) R.G.R. Bacou and S.C. Rennison, *Chem. Ind.* (London), **1966**, 812.