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The Reaction of Cadalene and Eudalene with Sulfur

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The action of sulfur on two naphthalenes was investigated. Cadalene was heated with sulfur to give a new sulfur-containing naphthalene, 1,5,8-trimethylnaphtho[2,1-*b*]thiophene. It was formylated at the C_2-position of the thiophene moiety according to the Vilsmeier procedure, while an attempted acetylation according to this procedure was unsuccessful. Similarly, the reaction of eudalene with sulfur gave 3,9-dimethylnaphtho[1,2-*b*]thiophene, whose structure was determined by chromium trioxide oxidation, yielding *o*-quinone, and by a subsequent reaction with *o*-phenylenediamine, forming a quinoxaline derivative.

In a previous investigation of the reaction of azulene with sulfur, it was shown that 3,5,8-trimethylazuleno[6,5-*b*]thiophene and 3,5,9-trimethylazuleno[1,2-*b*]thiophene were, respectively, obtained from *S*-guaiazulene[1,2] and vetivazulene,[3] and that 6- and 7-acetyl-3,5,8-trimethylazuleno[6,5-*b*]thiophenes were yielded from 3-acetylguaiazulene, which was also isomerized to 2-acetylguaiazulene through the acetyl migration.[4] The sulfur-containing product in these reactions commonly contains a β-methylthiophene ring formed between an azulene-ring carbon atom and the isopropyl side chain of the azulenes.

The present investigation is concerned with how the action of sulfur on cadalene and eudalene, both naphthalene derivatives containing isopropyl groups, gives two new sulfur-containing naphthalenes. The compound thus obtained from cadalene (I) was determined to be 1,5,8-trimethylnaphtho[2,1-*b*]-thiophene (II), whose structure corresponds to that of furanocadinene[5] except that its oxygen atom of a hetero-ring is replaced with a sulfur atom. Formylation and acetylation by electrophilic substitution on the compound were attempted according to the Vilsmeier procedure.[6] On the other hand, the compound from eudalene (VI) was determined to be 3,9-dimethylnaphtho[1,2-*b*]thiophene (VIIa). Another compound (VIIb), which was also to be expected from the structure of eudalene (VI), could not be found in this reaction, however.

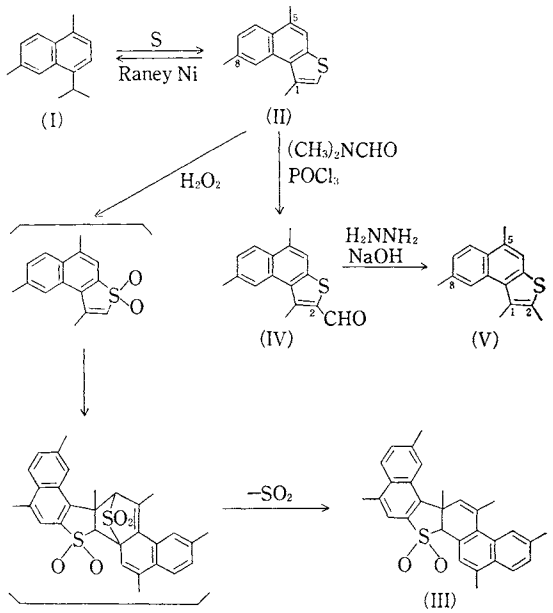


Chart 1

1) S. Hayashi, S. Kurokawa, M. Okano and T. Matsuura, *Tetrahedron Lett.*, **1967**, 3443.

2) S. Hayashi, M. Okano, S. Kurokawa and T. Matsuura, *J. Sci. Hiroshima Univ., Ser. A-II*, **31**, 79 (1967).

3) S. Hayashi, S. Kurokawa and T. Matsuura, This Bulletin, **42**, 1404 (1969).

4) S. Kurokawa, *ibid.*, **43**, 509 (1970).

5) H. Hikino, K. Agatsuma, C. Konno and T. Takemoto, *Tetrahedron Lett.*, **1968**, 4417.

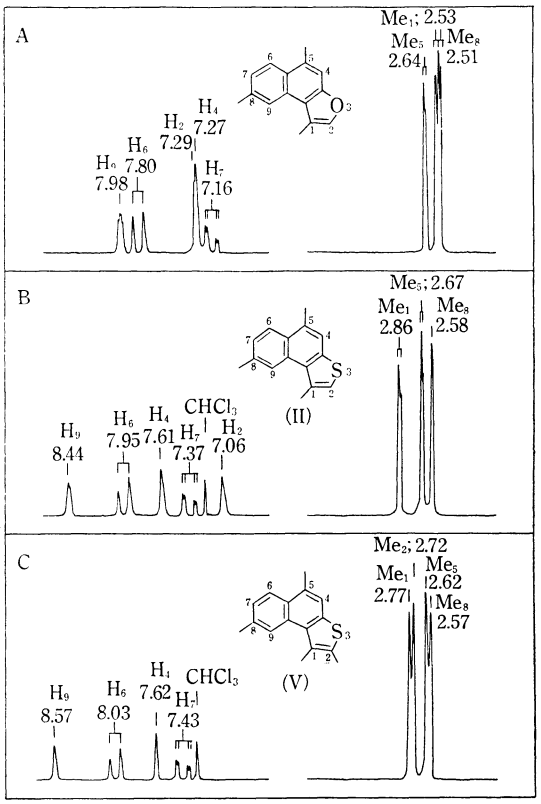
6) M.-R. de Maheas, *Bull. Soc. Chim. France*, **1962**, 1989.

Results and Discussion

The Structure of the Sulfur-containing Cadalene: 1,5,8-Trimethylnaphtho[2,1-*b*]thiophene. The heating of cadalene with sulfur at 260°C for 10 hr produced colorless needles, mp 148—150°C, as the main product.

This compound had the molecular formula of $C_{15}H_{14}S$, and was desulfurized by heating it with Raney nickel catalyst (W-2 type), thus regenerating cadalene in a good yield. Hence, it is certain that the compound retains a cadalene skeleton in its molecule. The UV spectrum of this compound has an absorption maximum at 245.5 mμ; this maximum is 14 mμ more on the bathochromic side than that of the original cadalene. This fact shows the compound to have an elongated conjugate system, and it can be deduced that the compound has the structure of II, which consists of a fused ring system of naphthalene and β-methylthiophene.

This structure was confirmed mainly by the NMR spectrometry as follows. In IR and NMR spectra of this compound, isopropyl signals, which are clearly observed in those of cadalene, are absent; three aromatic methyl signals (2.86, 2.67, and 2.58 ppm, each 3H), corresponding to an increase of one methyl group from those of cadalene, are present in the NMR spectrum (Fig. 1B).



← ppm from TMS

Fig. 1. NMR spectra of furanocadinene (A), 1,5,8-trimethylnaphtho[2,1-*b*]thiophene (B) and 1,2,5,8-tetramethylnaphtho[2,1-*b*]thiophene (C).

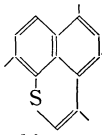
In the aromatic-proton region of the NMR spectrum we observed three singlet-like signals at 8.44, 7.61, and 7.06 ppm (precisely, multiplets), one doublet at 7.95 ppm (J=8.8 Hz), and one double doublet at 7.37 ppm (J=8.8 and 1.5 Hz). These aromatic proton signals can be reasonably assigned to H_9, H_4, H_2, and H_6 and H_7 in the structure (II)*1 on the basis of comparisons with the spectra of 3-methylcadalene[7] and benz[*b*]thiophene,[8] and from the results of a double-resonance experiment: irradiation of the double doublet at 7.37 ppm decoupled the doublet at 7.95 ppm.

The methyl signals mentioned above could also be ascribed to methyl groups of the formula (II), as is shown in Fig. 1B, on the basis of a comparison with the spectra of 3-methylbenz[*b*]thiophene,[8] azulenothiophenes,[1-4] and naphthalenes,[7] and on the basis of the results of the irradiation experiment on H_2, which decoupled the doublet at 2.86 ppm.

In structure (II) the oxygen atom of furanocadinene is replaced with a sulfur atom. In fact, the NMR spectrum of the present compound (Fig. 1B) is very close to that of furanocadinene (Fig. 1A), except for the well-known fact regarding a thiophene ring, that an α-H is more shielded, while a β-methyl group is more deshielded than that of a furan ring.[9]

Oxidation of 1,5,8-Trimethylnaphtho[2,1-*b*]-thiophene with Hydrogen Peroxide. In order to clarify the presence of a thiophene nucleus, the sulfur-containing compound was oxidized with hydrogen peroxide. A sulfone was obtained as pale yellow needles, mp 178—179°C, which had sharp absorption bands characteristic to ν_{SO_2} at 1292, 1276, and 1124 cm^{-1} in the IR spectrum. On the other hand, the NMR spectrum (Fig. 2) exhibits the presence of two aliphatic methyl (1.77 ppm, 6H) and four aromatic methyl groups [2.30 (d), 2.67 (s), 2.84 (s) and 3.23 ppm (s), each 3H], and a tri-

*1 If the NMR data concerning the aromatic proton region are neglected, an alternative structure,



must be also taken into account. However, this structure can now be excluded, for one singlet and four doublets would be expected as the aromatic proton signals.

7) B. A. Nagasampagi, S. Dev, C. Rai and K. L. Murthy, *Tetrahedron*, **22**, 1949 (1966).
8) J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, **1964**, 981.
9) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London (1959); Japanese translation by H. Shimizu, Tokyo-Kagaku-Dojin, Tokyo (1962), p. 95.

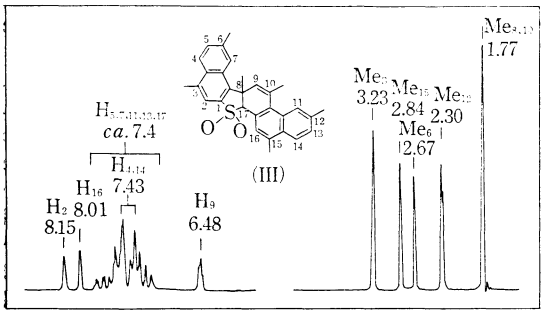


Fig. 2. NMR spectrum of the sulfone dimer (III).

substituted olefinic proton [6.48 ppm (m), 1H], in addition to eight aromatic protons showing complicated signals. Thus, this spectrum cannot be explained in terms of the simple sulfone to be expected from naphthothiophene (II).

In the hydrogen-peroxide oxidation of thiophene, Davies and James have observed that the sulfone, supposed to be the primary oxidation product, was condensed through Diels-Alder addition accompanied by the loss of sulfur dioxide.[10] In the oxidation of 1,5,8-trimethylnaphtho[2,1-*b*]thiophene, also, if its sulfone is thought to be dimerized similarly, structure (III) is possible; it explains well the above spectrometric evidence. The absorption maximum (236 mμ) of the UV spectrum is rather closer to that of cadalene (I) (232 mμ) than to that of naphthothiophene (II) (245.5 mμ). This fact also supports structure (III), which contains a shorter conjugate system than the original trimethylnaphthothiophene.

Electrophilic Substitution of 1,5,8-Trimethylnaphtho[2,1-b]thiophene (II). We attempted to acetylate naphthothiophene (II) with *N,N*-dimethylacetamide in the presence of phosphorus oxychloride, according to the Vilsmeier procedure, but the trial resulted only in the recovery of the starting material. This result is different from the cases of 3,5,8-trimethylazuleno[6,5-*b*]thiophene[4] and 3,5,9-trimethylazuleno[1,2-*b*]thiophene.[3]

On the other hand, a Vilsmeier formylation of the trimethylnaphthothiophene proceeded almost quantitatively to give a pale yellow crystalline substance, mp *ca.* 108°C, which showed an absorption band due to an aldehyde group at 1650 cm^{-1} in the IR spectrum and which furnished semicarbazone, mp 210°C (decomposition).

The crystalline aldehyde, upon Wolff-Kishner reduction,[11] gave a pale yellow crystalline substance, mp 130—131°C, which had a molecular formula of $C_{16}H_{16}S$, representing the increase of one methyl group as compared with the original trimethylnaphthothiophene.

When the NMR spectrum (Fig. 1C) is compared with that of the original compound (Fig. 1B), an aromatic proton signal corresponding to the H_2 (7.06 ppm) of the original compound is absent, and four aromatic methyl signals [2.77, 2.72, 2.62 and 2.57 ppm, each (s) and 3H] are seen, equivalent to an increase of one methyl group from the original trimethylnaphthothiophene. Besides, the methyl signal (2.77 ppm) attributable to Me_1 becomes a singlet in this compound, while it is a doublet in the trimethylnaphthothiophene.

These facts indicate that the introduction of the fourth methyl group, namely, the Vilsmeier formylation, took place at the C_2 position of the trimethylnaphthothiophene.

The Structure of the Sulfur-containing Eudalene: 3,9-Dimethylnaphtho[1,2-*b*]thiophene. The reaction of eudalene with sulfur gave colorless needles, mp 41.5—42.5°C, having a molecular formula of $C_{14}H_{12}S$. This compound regenerated eudalene when it was submitted to reductive desulfurization with a Raney nickel catalyst and successively dehydrogenated with palladium on charcoal. Hence, the compound certainly retains the eudalene skeleton in the molecule.

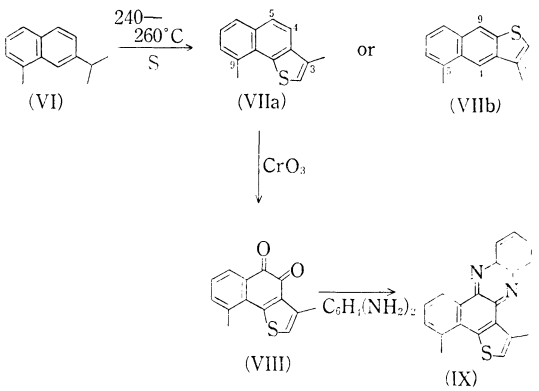


Chart 2

On the other hand, the participation of the isopropyl group of eudalene in the reaction with sulfur was indicated by the absence of splitting bands at 1382 and 1389 cm^{-1} in the IR spectrum and by the lack of NMR signals at 1.35 (doublet, 6H, J=6.7 Hz) and 3.05 ppm (multiplet, 1H) in Fig. 3A, as was seen in each spectrum of the starting material.

In the aromatic-methyl-proton region of the NMR spectrum (Fig. 3A), there is one more methyl doublet (2.52 ppm) than in the spectrum of the starting material, and the spin-coupling constant, J=1.0 Hz, of this newly-appeared doublet is in good agreement with the J value concerning the β-methyl group and the α-proton in 1,5,8-trimethylnaphtho[2,1-*b*]thiophene and in the other β-methyl-

10) W. Davies and F. C. James, *J. Chem. Soc.*, **1954**, 15.

11) H. Stetter and W. Dierichs, *Chem. Ber.*, **85**, 61 (1952).

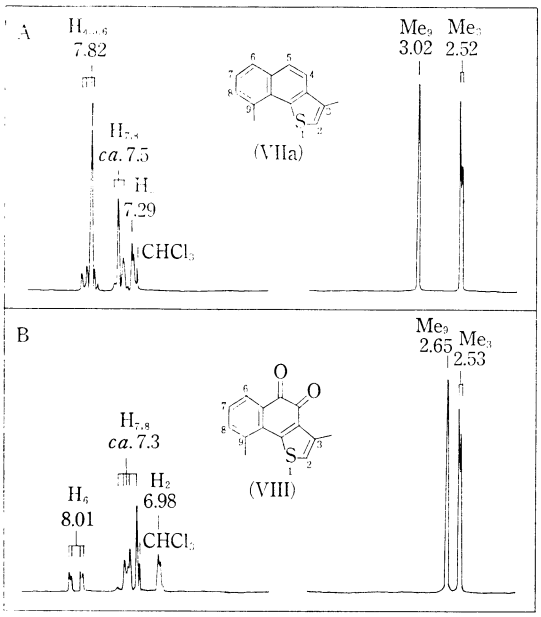


Fig. 3. NMR spectra of 3,9-dimethylnaphtho[1,2-*b*]thiophene (A) and its 4,5-quinone (B).

thiophenic compounds reported earlier.[1-4] Thus, this compound can also be concluded to be a naphthothiophene in which the isopropyl group and one of the aromatic-ring carbon atoms in eudalene forms a thiophene ring with sulfur, as in the reaction of cadalene or azulenes with sulfur. This deduction was powerfully supported by the prominent appearance of the $(M-1)^+$ ion (50.2%) in the mass spectrum of this compound, because the abundant formation of this ion is peculiar to methylthiophenes;[12] this ion can be described as a thiapyryrium ion formed through the expansion of a thiophene ring.

In this manner, two formulae, VIIa and VIIb become possible for the present compound. In order to determine the more reasonable structure of the two, the present compound was oxidized with chromium trioxide in glacial acetic acid to yield red needles, mp 206.5—207.5°C, as the main product. The red crystalline product exhibited $\nu_{C=O}$ bands at 1655 and 1667 cm^{-1} in the IR spectrum, showed two fewer proton signals in the aromatic-ring-proton region of the NMR spectrum (Fig. 3B) as compared with that of the dimethylnaphthothiophene (Fig. 3A), and had a molecular formula of $C_{14}H_{10}SO_2$ based on the parent ion ($M^+=242$) of the mass spectrum. This product is, therefore, a quinone yielded from the dimethylnaphthothiophene by the oxidation of one of two activated carbon positions, $C_{4,5}$ in VIIa or $C_{4,9}$ in VIIb. Besides, this red quinone had an intense absorption maximum at 466 mμ (log ε, 3.34) in the visible region, and in the NMR spectrum (Fig. 3B) the chemical shift between the two methyl groups ($\Delta Me_3-Me_{9\text{ or }5}=0.12$ ppm) is much smaller than that of the dimethylnaphthothiophene (0.50 ppm) (Fig. 3A). From the latter fact, the quinone can be deduced to have a structure in which Me_3 is closer to the carbonyl group than the other methyl group, Me_9 or Me_5. Thus, these data suggest that the product is not the *p*-quinone expected from VIIb, but *o*-quinone (VIII) of a phenanthraquinone type derived from VIIa.

Supporting this suggestion is the fact that this quinone reacted with *o*-phenylenediamine to form a greenish yellow powder, mp 202—203°C, which was determined to be a quinoxaline derivative (IX) derived from *o*-quinone (VIII) by elementary analysis and by a study of its mass spectrum. From the above evidence, it can be concluded that the colorless needles obtained by the reaction of eudalene with sulfur are 3,9-dimethylnaphtho[1,2-*b*]thiophene of a phenanthrene type; all the data other than those mentioned here support this structure.

Experimental

All the melting points in this paper are uncorrected. The IR spectra were obtained using KBr disks, and the mass spectra, at 70 eV. The NMR spectra were taken at 60 MHz in deuteriochloroform. The thin-layer chromatography (TLC) was carried out by the use of silica gel-G (Merck); unless otherwise stated, all the spots were detected by spraying with a mixture of sulfuric acid and nitric acid (19 : 1).

Reaction of Cadalene (I) with Sulfur. A mixture of cadalene (3.0 g) and sulfur (1.5 g) was heated at 260°C for 10 hr under a nitrogen atmosphere. The reaction mixture, which solidified at room temperature, was crushed into small fragments and ground thoroughly in a mortar with *n*-hexane to give a viscous red oil (0.6 g). This oil was then repeatedly chromatographed on a silica-gel column with *n*-hexane; a colorless crystalline substance (40 mg) (1,5,8-trimethylnaphtho[2,1-*b*]thiophene) was thus isolated. After two recrystallizations from *n*-hexane, it afforded colorless needles, mp 148.0—150.0°C, which showed a single green spot (R_f, 1.81) in TLC with petroleum ether. Mass spectrum: *m/e* 226 (M^+, $C_{15}H_{14}S$), base peak; *m/e* 225 $(M-H)^+$, 22.9%. Relative intensities of isotope ions: Found; M^+ (100), $(M+1)^+$ (17.38), $(M+2)^+$ (5.29%). Calcd for $C_{15}H_{14}S$; M^+ (100), $(M+1)^+$ (17.23), $(M+2)^+$ (5.70%). UV (isooctane): mμ (log ε), 220 sh (4.22), 235 sh (4.49), 245.5 (4.62), 259.5 (4.44), 298.5 (4.02), 306 (4.01), 319.5 (3.58), 334.5 (3.47).

Found: S, 14.46%. Calcd for $C_{15}H_{14}S$: S, 14.17%.

Desulfurization of 1,5,8-Trimethylnaphtho[2,1-*b*]thiophene (II). Trimethylnaphthothiophene (40.8 mg) was dissolved into absolute methanol (20 m*l*); the solution, after the addition of a W-2 Raney nickel catalyst (0.2 g) prepared freshly, was refluxed on a water bath. After 40 min, trimethylnaphthothiophene;

12) H. Bujikiewicz, C. Djerassi and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco (1964), p. 231.

the starting material, came to be hardly detected at all in TLC with *n*-hexane. Then the reaction mixture was filtered, washed with water, dried over anhydrous calcium chloride, and concentrated under reduced pressure to leave a colorless oil (50 mg). The oil exhibited a yellowish-green spot (R_f, 2.70) in TLC using *n*-hexane, together with a green spot (R_f, 1.62) attributable to unchanged trimethylnaphthothiophene. By means of preparative TLC, a colorless oil of R_f 2.70 was isolated; it was found to be identical with an authentic specimen of cadalene by UV and IR absorption spectrometry.

Hydrogen Peroxide Oxidation of 1,5,8-Trimethylnaphtho[2,1-b]thiophene (II). Formation of a Sulfone Dimer (III). A solution of trimethylnaphthothiophene (170 mg) in glacial acetic acid (1 m*l*) was mixed with 30% hydrogen peroxide (0.8 m*l*), and the mixture was refluxed on an oil bath for 20 min. The reaction mixture was then diluted with water (30 m*l*) and extracted with chloroform to give an orange, resinous material (200 mg). This material was chromatographed on a silica-gel column with chloroform; unchanged trimethylnaphthothiophene was recovered from a quickly-eluted fraction, and a yellow crystalline compound (71.1 mg) was obtained from the fraction next eluted. Further purification of the crystals by repeated elution chromatogaphy with mixed solvents of methylene chloride and chloroform (1 : 1 and 2 : 1) afforded a sulfone dimer (III) (26.2 mg) as pale yellow needles, mp 178—179°C. These crystals showed a single brown spot (R_f, 4.30) in TLC using a mixed solvent of methylene chloride and chloroform (7 : 3). UV (EtOH): mμ (log ε), 216 (4.82), 237.7 (4.95), 293 sh (4.09), 303 (4.13), 325 sh (3.81).

Vilsmeier Formylation of 1,5,8-Trimethylnaphtho[2,1-*b*]thiophene (II). To a solution of trimethylnaphthothiophene (125 mg) in *N*,*N*-dimethylformamide (4.2 m*l*), another solution of phosphorus oxychloride (0.42 g) in the same solvent (2.1 m*l*) was added under ice cooling. The mixture, after being allowed to stand at room temperature for 2 days, was heated at 60°C for 1 hr to complete the reaction, and then poured into water (160 m*l*). When the aqueous solution was made slightly alkaline by adding powdered sodium carbonate, followed by extraction with chloroform, a viscous yellow oil (255 mg) was obtained. Through the benzene-silica gel elution chromatography of the oil, 2-formyl-1,5,8-trimethylnaphtho[2,1-*b*]thiophene (114 mg) was separated as pale yellow needles, mp *ca.* 108°C, which showed a single reddish-orange spot (R_f, 5.40) in TLC with benzene when sprayed 2,4-dinitrophenylhydrazine.

Semicarbazone. From 2-formyl-1,5,8-trimethylnaphtho-[2,1-*b*]thiophene, semicarbazone was obtained as a crystalline mass; this mass gave colorless needles. mp 210°C (decomposition), after being recrystallized from ethanol. IR: $\nu_{C=O}$ splitting band at 1726 and 1717 cm^{-1}, ν_{N-H} 3470 cm^{-1}.

Reduction of 2-Formyl-1,5,8-trimethylnaphtho-[2,1-*b*]thiophene (IV). A mixture of formyltrimethylnaphthothiophene (211 mg), 100% hydrazine hydrate (160 mg), and powdered sodium hydroxide (377 mg) was heated at 200°C for 1.5 hr by which time the evolution of nitrogen gas had ceased. The reaction mixture, after being acidified with dilute hydrochloric acid, was extracted with chloroform; crude 1,2,5,8-tetramethylnaphtho[2,1-*b*]thiophene (V) (150 mg) was thus obtained as a reddish-orange crystalline mass, which was purified by means of benzene-silica gel elution chromatography. The purified pale yellow needles, mp 130—131°C (78 mg), showed a single green spot (R_f, 6.77) in TLC with benzene. Mass spectrum: *m/e* 240 (M^+, $C_{16}H_{16}S$), base peak; *m/e* 239 $(M-H)^+$, 22.8%; *m/e* 225 $(M-CH_3)^+$, 81.9%. Relative intensities of isotope ions: Found; M^+ (100), $(M+1)^+$ (17.96), $(M+2)^+$ (5.65%). Calcd for $C_{16}H_{16}S$; M^+ (100), $(M+1)^+$ (18.35), $(M+2)^+$ (5.70%).

Reaction of Eudalene (VI) with Sulfur. Eudalene (2.0 g) was heated with half as much powdered sulfur at 240—260°C for 6 hr. The reaction mixture was dissolved in hot benzene (100 m*l*) and poured into *n*-hexane (200 m*l*) to yield a brown precipitate. The solution, from which the precipitate had been filtered off, was then concentrated under reduced pressure to give a red oil (1.50 g). This oil was treated as has been described above for cadalene (I); a colorless crystalline substance (227.8 mg) was thus isolated. After recrystallization from methanol, dimethylnaphthothiophene (VIIa) was obtained as colorless needles, mp 41.5—42.5°C, which showed a single yellow spot (R_f, 5.8) in TLC with *n*-hexane. UV (EtOH): mμ (log ε), 238 sh (4.42), 245 (4.52), 259 sh (4.55), 266.2 (4.69), 283 (4.08), 294 (3.97), 305 (3.72).

Found: C, 79.19; H, 5.68; S, 15.04%. Calcd for $C_{14}H_{12}S$: C, 79.20; H, 5.70; S, 15.10%.

Desulfurization of 3,9-Dimethylnaphtho[1,2-*b*]-thiophene (VIIa). The reaction of dimethylnaphthothiophene (15.07 mg) with a Raney nickel catalyst was carried out in a manner similar to that used in the experiment described for 1,5,8-trimethylnaphtho[2,1-*b*]-thiophene (II). When the oil thus obtained (10 mg) was chromatographed on a silica-gel column with *n*-hexane, a colorless oil (7.6 mg) was separated in a pure state. It showed a single brown spot (R_f, 8.5) in TLC with *n*-hexane, and was clearly different from eudalene (R_f, 6.9). This substance may be concluded to be a partially hydrogenated eudalene on the basis of UV and the results of the following dehydrogenation experiment. UV (EtOH): mμ (log ε*[2]) 215.5 (4.02), 220 sh (3.99), 227 sh (3.66), 265 (2.62), 269.5 (2.71), 277.8 (2.70), 291 sh (1.96).

Dehydrogenation of the Desulfurized Product. The colorless oil (7.6 mg) obtained by the above desulfurization of dimethylnaphthothiophene (VIIa) was sealed in a glass tube with 5% palladium on charcoal (20 mg), and the tube was heated at 300°C for 10 min. After being cooled, the reaction mixture was dissolved in chloroform, the solution, from which the catalyst had been filtered off, was then concentrated under reduced pressure to give a colorless oil (50 mg). This oil was confirmed, by TLC with *n*-hexane, to be mainly composed of eudalene. A colorless oil purified by the use of preparative TLC was identical with eudalene (VI) in TLC and UV spectrometry.

Chromium Trioxide Oxidation of 3,9-Dimethylnaphtho[1,2-*b*]thiophene (VIIa). To a solution of the dimethylnaphthothiophene (209 mg) in glacial acetic acid (4.7 m*l*) we added, drop by drop another solution of chromium trioxide (350 mg) in 60% acetic acid (2.0 m*l*), after which the mixture was heated at 50—60°C for 1.5 hr. The reaction mixture was then poured into

*[2] These values were calculated on the assumption that MW=186.

water (53 m*l*) and extracted with chloroform. A viscous red material (250 mg) thus obtained was chromatographed on a silica-gel column with a mixed solvent of benzene-chloroform (2 : 1), a slightly yellow-colored, unchanged naphthothiophene (9.9 mg) fraction was eluted first, and then a red fraction. The red fraction gave, after the removal of the solvent, *o*-quinone (VIII) as red needles, mp 206.5—207.5°C (15.1 mg) which showed a single red spot (R_f, 2.5) in TLC (without any color reagent) when a benzene-chloroform (4 : 1) mixture was used. UV and visible absorption spectra (EtOH): mμ (log ε), 225 (4.39), 241 sh (4.13), 261 sh (4.19), 274 sh (4.33), 280 (4.37), 345.5 (3.71), 466 (3.34), 510 sh (3.17). Mass spectrum: *m/e* 242 (M^+, $C_{14}H_{10}SO_2$), 40.2%; *m/e* 214 $(M-CO)^+$ ($m^*=189.2$), base peak; *m/e* 186 $(M-2CO)^+$ ($m^*=161.7$), 10.4%; *m/e* 185 $(M-2CO-H)^+$, 33.1%.

Reaction of *o*-Quinone (VIII) with *o*-Phenylenediamine. *o*-Quinone (VIII) (8.1 mg) was heated with *o*-phenylenediamine (3.4 mg) on a steam bath for 10 min. At the end of this period, the reaction mixture was heated with ethanol (30 m*l*) and an insoluble part was filtered off. The hot ethanol solution was diluted with water (20 m*l*) and chilled overnight at −20°C; the precipitate of the quinoxaline derivative (IX) was obtained by filtration as a greenish-yellow powder, mp 202.0—203.0°C (2.9 mg). This powder showed a single yellow spot (R_f, 6.2) in TLC with a mixed solvent of chloroform-benzene (1 : 4). UV[*3]: mμ (log ε), 240 sh (4.57), 257 (4.83), 284.2 (4.49), 294.6 (4.52), 309 (4.46), 388 (4.22).

Found: N, 8.51%. Calcd for $C_{20}H_{14}SN_2$: N, 8.91%.

The author wishes to thank Professor Tamon Matsuura and Professor Shûichi Hayashi of Hiroshima University for their kind guidance and advice on this work. Thanks are also due to Professor Shô Itô of Tohoku University for his kind measurement of the NMR and mass spectra.

[*3] Ethanol containing 0.5% of chloroform was used as the solvent.