Desulfurization of Phenanthro[4,5-bcd]thiophene by Means of Methanol and a Molybdena Catalyst (1)

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Phenanthro[4,5-bcd]thiophene (1) is converted into phenanthrene (2) (50%) and a mixture of methylphenanthrenes (3) (12%) by means of methanol and a sulfided cobaltous oxide-molybdic oxide-aluminum oxide catalyst (CMA-1) at 450° in a flow system. Similarly, 2 gives 3; and 4-methylphenanthrene yields 2 plus 3 (main component 3-methylphenanthrene) under the same reaction conditions. Mechanisms of the reactions are discussed. A facile chromatographic separation for 1- and 4-keto-1,2,3,4-tetrahydrophenanthrenes is presented.

In continuation of our studies on the desulfurization of condensed thiophenes by means of a sulfided cobaltous oxide-molybdic oxide-aluminum oxide catalyst (CMA-1) plus methanol in a flow system we now report detailed results (4) from use of phenanthro[4,5-bcd]thiophene (1) as a substrate at 450°, a temperature at which dibenzothiophene undergoes desulfurization in 82% yield (5). Compound 1 has been tentatively identified as a component of the product mixture from hydrodesulfurization of

a: 1-isomer   d: 4-isomer
b: 2-isomer   e: 9-isomer
c: 3-isomer
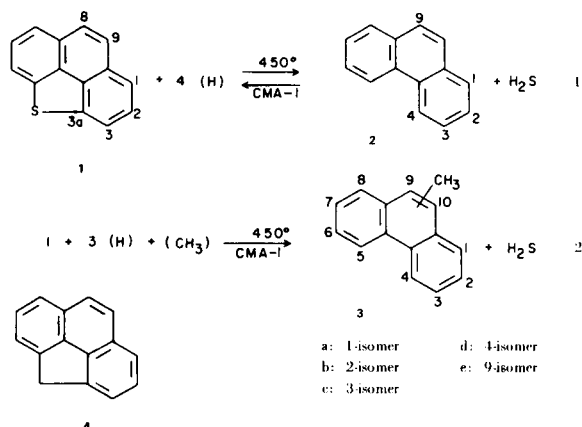
coal (6) and as a component (along with polycyclic aromatic hydrocarbons) of particulate environmental pollutants (7). Quantities sufficient for use in our studies were obtained from sulfur bridging of phenanthrene (2), a process developed in this laboratory (8,9).

In analogy to the dibenzothiophene system, desulfurization of 1 can be represented by equations 1 and 2, where equation 1 indicates that at 450° in the presence of CMA-1 the reaction can be driven either to the right (by means of methanol as an in situ source of hydrogen) or to the left (by means of hydrogen sulfide as reactant and carrier gas). Table I (runs 1 and 2) shows that yields of 2 (48-51%) and 3 (11-12%) are quantitatively reproducible, but that total mole percentage of hydrocarbons obtained (61 ± 2, by VPC analysis) is 20% lower than from dibenzothiophene (5) (10). Pmr analysis of the mixture of monomethylphenanthrenes obtained (11) shows the presence of only four of the five possible isomers. 4-Methylphenanthrene (3d) is missing. Moreover, 4,5-methylenephenanthrene (4) is not detected in the crude reaction mixture (12).

Runs 3, 4, and 7 are controls made on 2, 3d, and 4 (respectively) under reaction conditions almost identical
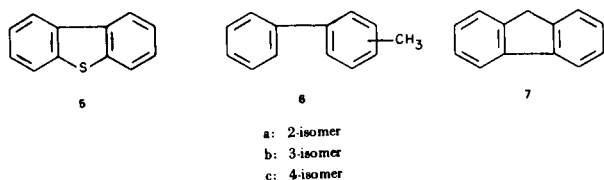
Table I

Transformations of Phenanthrene (2) and Derivatives with Methanol in a Flow Reactor at 450° (a)

| Run No. | Substrate | Catalyst or Packing | Yields, mole % | | | Isomeric Ratio (b) |
			2	3	4	3a:3b:3c:3d:3e
1 (c)	1	CMA-1	48	11	0	(d)
2	1	CMA-1	51	12	0	1.3:1.2:1.6:0:1.0
3	2	CMA-1	59	14	0	0.7:1.2:1.5:0:1.0
4	3d	CMA-1	28	18	5	0.8:0.9:7.1:3.4:1.0
5	2	sulfided alumina	(d)	ca. 0	ca. 0	-----
6	3d	glass beads	ca. 0	(d)	ca. 0	(e)
7	4	CMA-1	ca. 0	ca. 0	60	(f)

(a) Unless otherwise noted, each run was made with 0.5 g. of substrate, 75 ml. of methanol, and 37.5 g. of CMA-1 (or the equivalent bulk volume of other tube packing). Yields were determined by gas chromatography and relate directly to the moles of substrate used (rather than to the moles of products formed). (b) Determined by pmr analysis on the crude reaction mixture. (c) Run with twice the amounts given in (a). (d) Not determined. (e) No isomerization of 3d was observed. (f) Yields of 2 and 3 were determined as in (b).

with those of run 2. Some marked differences between analogous hydrocarbons in the phenanthrene and the biphenyl systems (5) are found, as noted in following paragraphs.

While biphenyl is recovered in 86% yield and only traces of methylbiphenyls are produced therefrom, phenanthrene recovery is less (59%) and monomethylation is appreciable (14%). The isomeric compositions of **3** formed from phenanthrothiophene **1** and phenanthrene (**2**) are nearly identical, except for the case of 1-methylphenanthrene (**3a**), which is approximately twice as abundant in the mixture from **1** as from **2**. A rationalization of this result is that some methylation occurs preferentially at C-1 (*para* to the sulfur atom in **1**) (13) prior to desulfurization, and (as shown for **2**) additional methylation occurs preferentially at C-3, C-2, and C-9 (in that order) after desulfurization. Run 5 (no reaction) shows that methylation of **2** cannot be ascribed to the presence of alumina *per se* in the CMA-1 catalyst.


a: 2-isomer
b: 3-isomer
c: 4-isomer

Absences of **3d** and 2-methylbiphenyl (**6a**) [amongst isomers **6a-6c**] in the reaction mixtures from **1** and dibenzothiophene (**5**), respectively (5), with CMA-1 at 450° appear analogous. Both **6a** and **3d** are unstable under these reaction conditions. They differ, however, in the products into which they are transformed. While **6a** readily undergoes dehydrocyclization to produce fluorene (**7**) (68%) [with little attendant isomerization (*ca.* 1%) or demethylation (4%)]; **3d** (run 4) gives mainly demethylation (28%) to **2** and accompanying isomerization (15%), plus limited dehydrocyclization (5%) to **4**. The distribution of isomers amongst the methylphenanthrenes produced is consistent with the combined operation of two mechanistic pathways, *viz*. (a) successive steps of demethylation to **2** plus re-methylation and (b) direct methyl migration from C-4 to C-3 (to yield **3c**). It is significant that **2**, **3c**, **4**, and **7** are all thermally stable up to 750° (14). Run 6 shows that **3d** is also thermally stable at 450°. Thus, it is clear that the transformations of **3d** found in run 4 are catalyzed rather than thermal.
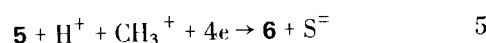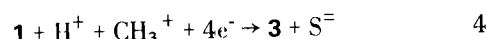
The electronic nature of the methyl group which attacks **1** or **2** is uncertain at this time. Substitution reactions of the phenanthrothiophene system **1** have not yet been reported (13). Phenanthrene is more reactive than biphenyl in attack by methyl free radicals (15), but the isomeric ratio in the resultant **3** apparently has not been determined. Assuming that this ratio will be the same as in free-radical phenylation (16), one expects a distribution of (**3a** +

3e):**3b**:**3c**:**3d** = 56.0:7.5:10.2:25.7 (17). After correction for re-distribution of methyl groups from C-4 (as per our run 4) the predicted ratio would be (**3a** + **3e**):**3b**:**3c** = 6.1:1.0:2.9, markedly different from the ratio of 1.9:1.0: 1.3 found in run 2. In closer agreement with the ratio found in run 2 are the results from electrophilic cyclohexylation of **2** by thermal decomposition of cyclohexyl benzenesulfonate at 115° (18), namely 1-:2-:3-:4-:9- = 0.85:1.0:1.57:0:2.0 in substituent distribution. In fact, the methyl group in run 2 shows less selectivity in its substitution pattern on **2** than does the bulkier cyclohexyl group. Such a steric effect on isomer distribution has been noted in alkylation of naphthalene with various alkyl arenesulfonates (18).

The balanced substrate half-reaction for the conversion **1 → 2** is shown in equation 3. Thus, the CMA-1 catalyst

$$1 + 2H^+ + 4e^- \rightarrow 2 + S^= \qquad\qquad 3$$
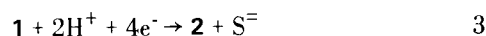
may be considered to function as a "coupled proton-electron transfer" agent, as has been proposed for the catalytic role of molybdenum enzymes (19). Analogously the balanced substrate half-reactions for the conversions **1 → 3** and dibenzothiophene (**5**) **→ 6** are presented in equations 4 and 5, respectively, where the catalyst adopts the dual

$$1 + H^+ + CH_3^+ + 4e^- \rightarrow 3 + S^= \qquad\qquad 4$$

$$5 + H^+ + CH_3^+ + 4e^- \rightarrow 6 + S^= \qquad\qquad 5$$

role of coupled electron-proton and electron-methyl carbonium ion transfer agent. As in organic electrochemistry, then, the products formed and the apparent electronic natures of the interacting species (e.g. the action of the methyl group as a carbonium ion, a free radical, or a carbanion) will depend on the sequence of steps which prevail (20). Differences noted (in our desulfurization studies) between the dibenzothiophene-biphenyl system and the phenanthrothiophene-phenanthrene system may result from different sequential processes in the two cases (21).

4-Methylphenanthrene (**3d**), used as a substrate and reference compound in our study, was synthesized from naphthalene by a modification of the Haworth-Bachmann five-step procedure (22-24). From the first step in this synthetic route one obtains a mixture of the isomeric β-(1- and 2-naphthoyl)propionic acids (**8a** and **8b**). Haworth
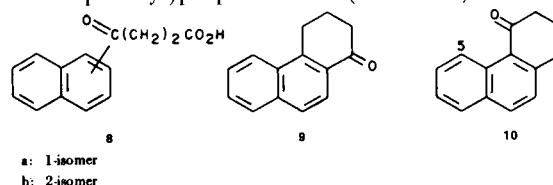
a: 1-isomer
b: 2-isomer

effected a separation of this mixture by crystallization, while Newman *et al.* (25) accomplished the separation by

means of fractional precipitation upon stepwise acidification of a basic solution of **8**. Only isomer **8b** was then used to produce intermediate 4-keto-1,2,3,4-tetrahydrophenanthrene (**10**), on the pathway to **3d**. In our study we found that both methods of separation were tedious, capricious, and unsatisfactory. Notable success was achieved, however, by delaying the separation of isomers until after the third step. Thereupon, the mixture of isomeric ketones **9** and **10** was readily separated by column chromatography with silica gel and benzene. As expected for adsorption by hydrogen bonding between the silica gel surface and the carbonyl group of the adsorbate, the 4-keto isomer (**10**) [greater steric hindrance to hydrogen bonding] is eluted faster than the 1-keto isomer (**9**) (26).

Both Haworth and Newman *et al.*, used melting points to assess the effectiveness of separation of isomers **8a** and **8b**. This criterion appeared to be unreliable in our study, since a sample of **8** of m.p. 173-176° (presumed to be pure **8b**) was, in fact, transformed into a mixture of chromatographically separable ketones **9** and **10**. Separations of these ketones, in contrast, can be readily and effectively monitored; both qualitatively by tlc and quantitatively by pmr spectrometry.

EXPERIMENTAL (27)

Chromatographic Separation of 1- and 4-keto-1,2,3,4-tetrahydrophenanthrenes (**9** and **10**).

A mixture of **9** and **10** (b.p. 150-160°/0.1 mm.) was synthesized from naphthalene by the Haworth procedure (22), as modified by Bachmann and Struve (23). Thin layer chromatography of this mixture on silica gel F-254 with benzene as eluent showed two spots (detected in ultraviolet light at 254 nm): **9**, R_f 0.30, violet color which appeared immediately after drying the plate; **10**, R_f 0.45, grey-black color which developed 1-3 minutes later. Based on the tlc results, macroscale separation of isomers was effected by column chromatography. A solution of 6.5 g. of mixed isomers in 10 ml. of benzene was admixed with 10 g. of silica gel (J. T. Baker No. 3405, 60-200 mesh) and the solvent was removed by rotoevaporation. The residue was added to the top of a column (4.5 cm. i.d. x 90 cm. in length) of dry-packed silica gel (650 g.), covered with a layer of sand, and eluted with benzene. Separation was monitored by means of ultraviolet light at 366 nm for observation of the column, plus tlc (observed at 254 nm) of the effluent fractions. Eluted (in order) from the column were impurities (0.2 g.) in the first 400 ml. of effluent; **10** (2.6 g.), observed as a dark band on the column; a mixture of **9** and **10** (0.9 g.), overlapping zones; and **9** (2.5 g.), observed as a light-blue band. Elution of **9** was hastened by use of 500 ml. of acetone in place of benzene for the last fraction. Combined fractions (7.9 g.) of **10** from three columns were recrystallized from 9 ml. of 95% ethanol to yield 6.9 g. of platelets, m.p. 67-68°; reported prisms, m.p. 69-70° (24). Likewise, recrystallization of 7.6 g. of **9** from 100 ml. of ethanol gave 5.9 g. of needles, m.p. 94-95.5°; reported 95-96° (28a). The pmr spectra of these ketones were consistent with published data (29). Especially distinctive in the spectrum of **10** is the low-field signal (δ 9.3-9.6 ppm) for H-5.

After considerable effort a batch of β-naphthoylpropionic acid (m.p. 173-176°) was separated from the mixed 1- and 2-isomers (30) by a modification of the procedure of Newman, *et al.*, (25).

Treatment of this sample by the method of Bachmann and Struve (23) plus chromatography (as indicated above) gave both **9** and **10** (ratio 0.6:1.0), plus impurities.

Hydrocarbon Reference Compounds.

1-, 2-, and 3-Methylphenanthrenes (**3a-3c**) and 4,5-methylenephenanthrene (**4**) were available from Aldrich Chemical Co., Milwaukee, Wis. 4-Methylphenanthrene (**3d**) was synthesized from ketone **10** by a literature procedure (24); purified by crystallization of the picrate (m.p. 140-141° from absolute ethanol) (28b), dissociation of the picrate by chromatography with alumina and chloroform, and evaporative distillation of the recovered eluate at 0.3 mm. to give crystals, m.p. 48.5-50°; reported m.p. 49-50° (24). 9-Methylphenanthrene (**3e**) was synthesized from 9-bromophenanthrene by the procedure of Bachmann (31), purified *via* the picrate [m.p. 151-153°; reported 152-153° (28b)], and recrystallized from methanol: m.p. 88-89°; reported, 90-91° (31).

The pmr spectra of these reference compounds are as follow: **3a**, δ 2.76 (s, 3, methyl group), 7.3-8.1 (m, 7 aromatic H), 8.5-8.8 ppm (m, 2, H-4 and H-5); **3b**, δ 2.55 (s, 3, methyl group), 7.3-8.0 (m, 7 aromatic H), 8.4-8.8 ppm (m, 2, H-4 and H-5); **3c**, δ 2.61 (s, 3, methyl group), 7.3-8.0 (m, 7 aromatic H), 8.48 (broad s, 1, H-4), 8.57-8.8 ppm (m, 1, H-5); **3d**, δ 3.15 (s, 3, methyl group), 7.4-8.1 (m, 8 aromatic H), 8.8-9.1 ppm (m, 1, H-5); **3e**, δ 2.74 (s, 3, methyl group), 7.4-8.2 (m, 7 aromatic H), 8.5-8.9 ppm (m, 2, H-4 and H-5); **4**, δ 4.29 (s, 2, methylene group), 7.4-8.0 ppm (m, 8, aromatic H). Examination of the methyl group singlet for 9-methylphenanthrene (**3e**) at an expanded scale width of 250 Hz showed splitting into a doublet, J = 1.2 Hz.

General Procedure and Analysis of Products Formed.

The general methodology of conducting reactions in a packed flow-reactor tube and of investigating products formed was described previously (5). Isomeric monomethylphenanthrenes were not separated by VPC either on a Carbowax or a mixed nitrate column, but were treated as a single peak of **3**. When this peak was isolated from the latter column (run 2) it showed no evidence for the presence of extraneous components by pmr or high resolution mass spectrometry (Exact mass: Calcd. for $C_{15}H_{12}$, 192.094; Found: 192.095). Isomeric ratios present in **3** were determined on crude reaction mixtures by careful pmr analysis of the methyl resonances in the region of δ 2-3.5 ppm. This analysis involved expansion of the scale width to 250 Hz, amplification of the signals to nearly full scale, and integration of the resultant signals: (in order of increasing δ values) C-2 methyl singlet, C-3 methyl singlet, C-9 methyl doublet, C-1 methyl singlet, and (in run 4 only) C-4 methyl singlet. Quantitative analysis for 4,5-methylenephenanthrene in crude reaction mixtures was effected by pmr integration of the methylene signal at 4.29 ppm (32).

REFERENCES AND NOTES

(1) This investigation was supported by research grant no. MPS 75-04116 from the National Science Foundation. For Paper VI in this series see L. H. Klemm and J. J. Karchesy, *J. Heterocyclic Chem.*, **15**, 281 (1978).

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(3) Research Assistant, 1977-.

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(10) At this point no effort has been made to establish reaction conditions which provide maximal total yields of desulfurized products from **1**.

(11) The gas chromatogram indicates the formation of no more than trace amounts of dimethylphenanthrenes.

(12) If more than a trace amount of either **3d** or **4** were present in the crude reaction mixture it should have been readily detected by pmr analysis (See Experimental).

(13) A simple Hückel molecular orbital calculation of superdelocalizabilities shows that **1** should undergo both electrophilic and free radical attack preferentially at C-1 and C-3 and nucleophilic attack preferentially at C-8 (equivalent to C-9). We thank Prof. C. E. Klopfenstein of our faculty for this calculation.

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(32) It is interesting to note that B. J. Mair and J. L. Martinez-Pico [*Proc. Am. Petrol. Inst., Sect. III*, **42**, 173 (1962)] established the presence of four monomethylphenanthrenes (**3a**, **3b**, **3c** and **3e**) in a trinuclear aromatic portion of heavy gas oil and light lubricating distillate by means of pmr analysis. No **3d** was detected, even though its presence was carefully sought. The absence of an identifying signal for **4** in their fractions is surprising, particularly since this compound (along with **3a**, **3b**, **3c** and **3e**) has been identified in coal tar [O. Kruber, *Ber.*, **67**, 1000 (1934); O. Kruber and A. Marx, *ibid.*, **71**, 2478 (1938); C, Karr, P. A. Estep, T. L. Chang and J. R. Comberiati, *U.S. Bur. Mines Bul.*, **637**, (1967)].