210° (sand bath) under nitrogen for 2 h. At the end of this time an oil was observed above the sand level. The tube was cut below this level and the oil was washed into a flask with chloroform which was removed in vacuo leaving 3*H*-2,1-benzoxathiole 1-oxide (138 mg, 0.9 mmol, 90%) whose properties were identical with those reported above.

Reduction of Benzothiete 1,1-Dioxide with Lithium Aluminum Hydride. Benzothiete 1,1-dioxide (154 mg, 1 mmol) was dissolved in 10 ml of dry tetrahydrofuran (THF). This solution was added dropwise to a stirred suspension of lithium aluminum hydride (156 mg, 4 mmol) in THF (5 ml) at 0 °C. The mixture was quenched with H_2O (0.2 ml) and 3 N NaOH (0.2 ml). To this was added 3 N NaOH (3 ml) and diethyl ether (25 ml). The solid was removed by filtration and the layers were separated. The aqueous layer and solid were acidified with 10% hydrochloric acid and extracted twice with 10 ml of chloroform. The extracts were dried and the solvent removed in vacuo. The residue was submitted to dry column chromatography (silica gel, chloroform eluent). *o*-Toluenethiol (70 mg, 0.56 mmol, 56%) was obtained as a pale yellow oil: ir (film) 2600 (w), 1460 (s), 745 cm^{-1} (s); NMR ($CDCl_3$) δ 7.08 (m, 4 H), 3.32 (s, 1 H), 2.25 (s, 3 H). The ir and NMR spectra were identical with those reported for an authentic sample of *o*-toluenethiol.[22]

Acknowledgment. The authors are grateful to the National Cancer Institute (Grant CA 08250) for support of this work.

Registry No.—**1**, 5687-92-3; **2**, 59463-72-8; **3**, 59463-73-9; **4**, 59463-74-0; **5**, 59463-75-1; **6**, 16065-50-2; butadiene, 106-99-0; 3*H*-2,1-benzoxathiole 1-oxide, 31910-65-3; *o*-toluenethiol, 137-06-4.

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A Thiophene Analogue of 7,12-Dihydropleiadene

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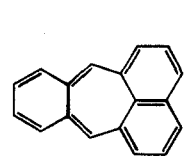
Replacement of the benzene ring in pleiadene (**1**) by a *b*-fused thiophene ring gives rise to the analogue naphtho[1,2-*b*]thiophene[1] (**2a**) as shown. Pleiadene itself has been gener-



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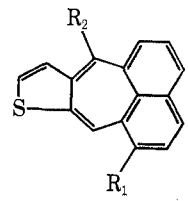
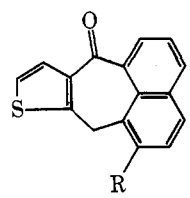
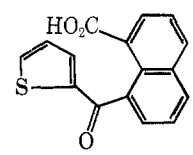


2a, $R_1 = R_2 = H$
b, $R_1 = OCH_3$; $R_2 = OCOCH_3$
c, $R_1 = OCH_3$; $R_2 = OK$



3a, R = H
b, $R = OCH_3$



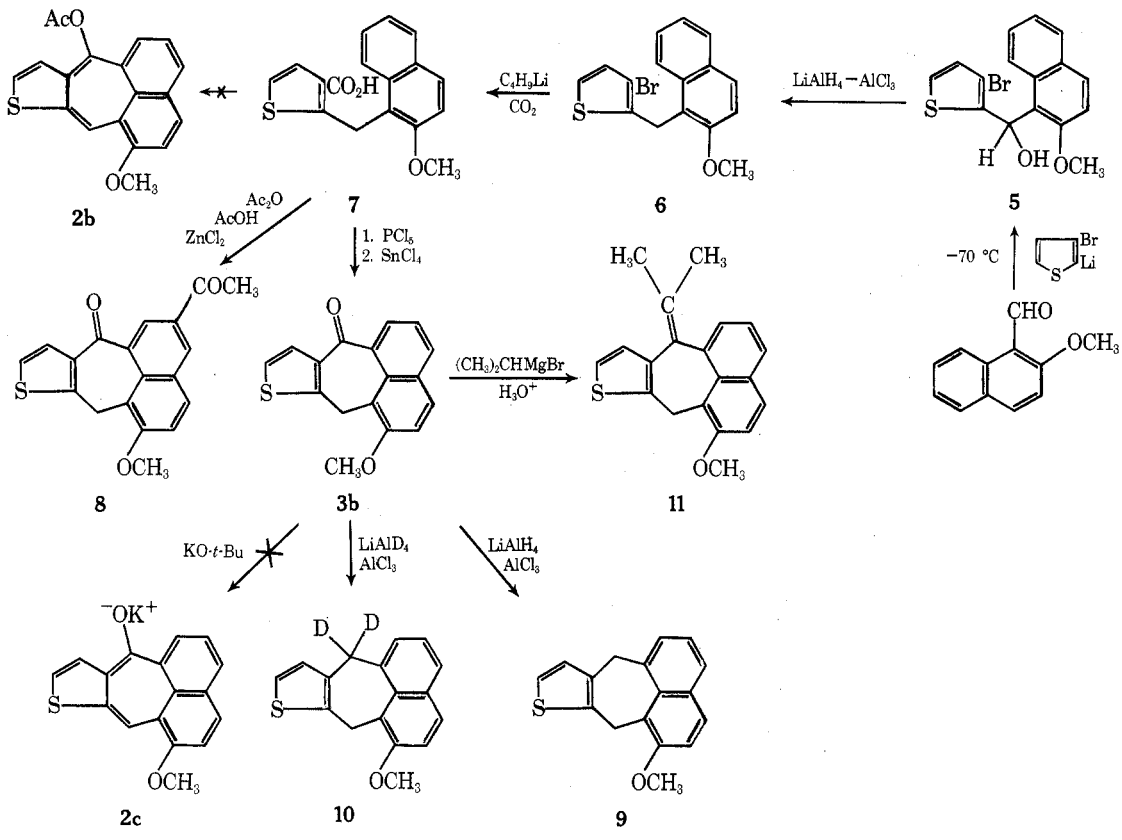
4

ated in solution by Cava and co-workers[2] and has been shown to undergo an addition reaction with *N*-phenylmaleimide and also to dimerize. The present work reports an attempt to ascertain if any quinodimethane character can be detected in a keto analogue of **2**, viz., **3b**. Attempts to utilize 8-(2-thenoyl)-1-naphthoic acid (**4**) (as a precursor for **3a**) were abandoned owing to difficulty in reducing the ketone group and the scheme outlined below was followed.

Reaction of 2-methoxy-1-naphthaldehyde with 3-bromo-2-thienyllithium at −70 °C afforded 1-(2-methoxynaphthyl)-3′-bromo-2-thienylmethanol (**5**) in 62% yield. Reduction of the alcohol function by means of lithium aluminum hydride–aluminum chloride[3] gave 1-(3′-bromo-2′-thenyl)-2-methoxynaphthalene (**6**) in 52% yield. The bromo derivative **6** was converted to the corresponding carboxylic acid **7** in 91% yield by treatment with *n*-butyllithium at −70 °C followed by carbonation. Cyclization of the resulting 1-(3′-carboxy-2′-thenyl)-2-methoxynaphthalene (**7**) by means of phosphorus pentachloride followed by stannic chloride gave the cyclic ketone 6-methoxynaphtho[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophen-11(7*H*)-one (**3b**) in 68% yield.

An attempt to form the pleiadene analogue 11-acetoxy-6-methoxynaphtho[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophene (**2b**) by treatment of the acid **7** with acetic anhydride and zinc chloride under conditions where acetoxyanthracenes were produced[4] afforded a product whose spectra and elemental analysis indicated it to be 2-(?)-acetylmethoxynaphtho-[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophen-11(7*H*)-one (**8**), together with unreacted starting material. When the above reaction was carried out in the presence of *N*-phenylmaleimide in an attempt to trap **2b**, only unchanged starting material was recovered.

An attempt was made to ascertain whether base-catalyzed enolization of **3b** could be induced by treatment of the ketone with freshly sublimed potassium *tert*-butoxide.[6] Upon mixing these reagents in THF solution no change in color was observed. Quenching of the mixture with deuterium oxide re-



sulted in a quantitative recovery of starting material with no deuterium incorporation as shown by NMR spectroscopy. This result indicates the absence of any species such as **2c.**

The ketone **3b** upon treatment with lithium aluminum hydride and aluminum chloride in refluxing ether gave 6-methoxy-7,11-dihydronaphtho[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophene (**9**) in 56% yield. A study of the NMR spectrum of **9** showed no evidence of coupling between the 7 and 11 hydrogen atoms at room temperature because of the rapid inversion of the seven-membered ring. At −74 °C the two signals for the nonequivalent methylene protons coalesced to a broad hump. Further cooling to −90 °C caused this broad hump to split into four signals: $J_{AA'}$ = 17 Hz, $J_{BB'}$ = 27 Hz; δ (measured from OCH_3) δ_A = 39 Hz, δ_B = 25 Hz at −90 °C; δ_A = 37 Hz, δ_B = 25 Hz at 25 °C. The 11,11-dideuterio compound **10,** prepared from **3b** by reduction with lithium aluminum deuteride–aluminum chloride, showed a splitting of the singlet into a clearly resolved doublet at −86 °C, J = 16 Hz, coalescence temperature −77 ± 1.5 °C.

Reaction of the ketone **3b** with isopropylmagnesium bromide followed by acid-catalyzed dehydration afforded 6-methoxy-11-isopropylidene-7,11-dihydronaphtho[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophene (**11**) which showed an AB quartet for the seven methylene protons with J_{AB} = 16 Hz and $\Delta\nu_{AB}$ = 34 Hz, which also paralleled the results found for 7-isopropylidene-7,12-dihydropleiadene.[5]

It is thus seen that the NMR spectral behavior of **9, 10,** and **11** is similiar to that of the analogous dihydropleiadene derivatives except that the coalescence temperatures for inversion of **9, 10,** and **11** are much lower than for 7,12-dihydropleiadene[5]—about −75 °C as compared to 8 °C. A more rapid inversion of the seven-membered ring in the thiophene series is indicated.

It has not been found possible to prepare derivatives of **2** analogous to **1.**

Experimental Section[7]

1-(2-Methoxynaphthyl)-3′-bromo-2′-thienylmethanol (5). To a solution of *n*-butyllithium in ether (110 ml, 1.76 M, 0.194 mol) cooled to −70 °C was added a solution of 2,3-dibromothiophene (46.8 g, 0.194 mol) in 30 ml of ether. After stirring for 30 min at −70 °C, 2-methoxynaphthaldehyde[8] (36.1 g, 0.22 mol) in 200 ml of 1:1 ether–benzene was added. The mixture was stirred for 5 h during which it was allowed to warm to 10 °C. Addition of ammonium chloride solution followed by extraction with ether, washing, and drying ($MgSO_4$) gave a deep green colored oil (64.7 g). Chromatography on alumina (900 g) with chloroform as eluent afforded a light yellow oil, 60 g (88%), which yielded colorless needles from cyclohexane: mp 74.5–75 °C; 40 g (62%); ir (CCl_4) 3450 cm^{-1}; NMR (CCl_4) δ 6.8–8.0 (m, 8 H, aromatic), 6.6 (s, H, CH), 4.0 (s, 1 H, OH), 3.8 (s, 3 H, OCH_3). Anal. Calcd for $C_{16}H_{13}BrO_2S$: C, 55.02; H, 3.75; S, 9.18. Found: C, 54.79; H, 3.90; S, 8.96.

1-(3′-Bromo-2′-thenyl)-2-methoxynaphthalene (6). To a suspension of lithium aluminum hydride (1.9 g, 0.05 mol) in anhydrous ether (50 ml) was added with cooling aluminum chloride (6.7 g, 0.05 mol) in anhydrous ether (2000 ml). To this mixture was added dropwise 9.7 g (0.028 mol) of 1-(2-methoxynaphthyl)-3-bromothienylmethanol (**5**) in 50 ml of ether over a period of 30 min. The mixture was heated under reflux for a further 30 min and was then decomposed by the cautious addition of 3 M H_2SO_4. Addition of water followed by extraction with ether, washing, and drying ($MgSO_4$) gave, upon removal of the ether, a yellow oil (8.8 g) which upon chromatography over alumina (170 g) with hexane as eluent gave a colorless oil which crystallized upon standing to white prisms. Recrystallization from hexane afforded large white cubes: 4.8 g (52%); mp 73–73.5 °C; ir (KBr) 3070, 2930 cm^{-1}; NMR (CCl_4) δ 6.8–8.0 (m, 8 H, aromatic), 4.5 (s, 2 H, CH_2), 3.9 (s, 3 H, OCH_3). Anal. Calcd for $C_{16}H_{13}BrOS$: C, 57.66; H, 3.93; S, 9.62. Found: C, 57.85; H, 4.03; S, 9.40.

1-(3′-Carboxy-2′-thenyl)-2-methoxynaphthalene (7). To a solution of ethereal *n*-butyllithium (8 ml, 0.013 mol) cooled to −70 °C under nitrogen was added 1-(3′-bromo-2-thenyl)-2-methoxynaphthalene (**6,** 3.3 g, 0.011 mol) in 50 ml of ether. The mixture was stirred for 30 min at −70 °C and was then poured onto an excess of dry ice (100 g) and allowed to come to room temperature. Addition of 1 M HCl (50 ml) followed by extraction with ether gave upon removal of the solvent a white solid which was recrystallized from 1:1 benzene–hexane to give the acid **7,** 2.7 g (83%), mp 175–177 °C. An additional recrystallization gave an analytical sample: mp 176.2–177 °C; ir (KBr) 3450, 1665 cm^{-1}; NMR (acetone-d_6) δ 6.6–7.6 (m, 8 H, aromatic), 4.6 (s, 2 H, CH_2), 3.5 (s, 3 H, OCH_3). Anal. Calcd for $C_{17}H_{14}O_3S$: C, 68.43; H, 4.73; S, 10.75. Found: C, 68.30; H, 4.77; S, 10.61.

6-Methoxynaphtho[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophen-11(7*H*)-one (3b). To a stirred suspension of the acid **7** (2.98 g, 10

mmol) in dry benzene (25 ml) at 5 °C was added phosphorus pentachloride (2.08 g, 10 mmol) over a 10-min period. When evolution of hydrogen chloride had ceased, the solution was cooled to 4 °C and a solution of stannic chloride (3.35 g, 13 mmol) in benzene (50 ml) was added dropwise with stirring over a 30-min period. The magenta colored mixture was allowed to warm up to room temperature and was stirred for 2 h. Decomposition of the complex with 0.1 M HCl and ice, followed by benzene extraction with washing and drying ($MgSO_4$), gave, upon removal of the solvent, a yellow oil. This was chromatographed on silica gel using 3:1 benzene–chloroform as eluent to give yellow crystals (1.9 g, 68%) mp 161–162 °C. An analytical sample (mp 162.5–163 °C) was obtained by recrystallization from benzene–hexane as bright yellow prisms with a brilliant green fluorescence: ir (KBr) 1625 cm^{-1}; NMR (Unisol-D) δ 7.0–8.3 (m, 8 H, aromatic), 4.6 (s, 2 H, CH_2), 4.0 (s, 3 H, OCH_3). Anal. Calcd for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.32; S, 11.43. Found: C, 73.09; H, 4.25; S, 11.60.

Attempted Synthesis of 11-Acetoxy-6-methoxynaphtho[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophene (2b). A stirred mixture of 1-(3′-carboxy-2′-thenyl)-2-methoxynaphthalene (**7**, 1.0 g, 3.36 mmol), acetic anhydride (25 ml), acetic acid (20 ml), and freshly fused zinc chloride (1.2 g, 8.8 mmol) was heated under reflux for 0.5 h. To the hot solution was added water (25 ml) dropwise and the reaction mixture was cooled in ice. Yellow needles separated and were removed by filtration (0.8 g, 71%), mp 207–208.5 °C. This substance gave a positive iodoform test. Recrystallization from benzene–hexane followed by sublimation in vacuo gave **8** as pale yellow needles: mp 208–208.5 °C; ir (KBr) 1660 (C=O), 1645 cm^{-1} ($ArCOCH_3$); NMR (acetone-d_6) δ 7.5–6.9 (m, 7 H, aromatic), 4.55 (s, 2 H, CH_2); 4.0 (s, 3 H, OCH_3), 2.45 (s, 3 H, $COCH_3$). Anal. Calcd for $C_{19}H_{14}O_3S$: C, 70.79; H, 4.38; S, 9.95. Found: C, 70.59; H, 4.35; S, 10.06.

6-Methoxy-7,11-dihydronaphtho[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophene (9). To a cooled, stirred suspension of lithium aluminum hydride (0.23 g, 6.0 mmol) in ether (25 ml) was added, with cooling and stirring, a solution of aluminum chloride (0.80 g, 6 mmol) in 25 ml of anhydrous ether. To this was added a solution of 6-methoxynaphtho[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophen-11(7*H*)-one (1.0 g, 3.5 mmol) in ether (35 ml). The mixture was stirred under reflux for 16 h. Careful addition of 5% H_2SO_4 followed by extraction with ether, washing with $NaHCO_3$, and drying ($MgSO_4$) gave upon removal of the solvent a white solid (0.5 g, 54%), mp 130–132 °C. Sublimation gave an analytical sample: mp 129–130 °C; NMR ($CDCl_3$) δ 6.9–7.8 (m, 7 H, aromatic), 4.7 (s, 2 H, CH_2), 4.4 (s, 2 H, CH_2), 4.0 (s, 3 H, OCH_3). Anal. Calcd for $C_{17}H_{14}OS$: C, 76.66; H, 5.30; S, 12.04. Found: C, 76.41; H, 5.31; S, 12.13.

6-Methoxy-11,11-dideuterio-7,11-dihydronaphtho-[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophene (10). From the ketone **3b** (2.0 g), lithium aluminum deuteride (1.0 g), and aluminum chloride (32 g) there was obtained 1.85 g (98%) of **10**: mp 129.5–130 °C; NMR ($CDCl_3$) δ 6.8–7.7 (m, 7 H, aromatic), 4.6 (s, 2 H, CH_2), 3.9 (s, 3 H, OCH_3); mol wt by mass spectrum, 268 (calcd for $C_{17}H_{12}D_2OS$, 268).

6-Methoxy-11-isopropylidene-7,11-dihydronaphtho[1′,8′:4,5,6]cyclohepta[1,2-*b*]thiophene (11). To a filtered ethereal solution of isopropylmagnesium bromide from isopropyl bromide (12.37 g, 0.1 mmol) and magnesium (2.67 g, 0.11 g-atom) was added a solution of 1.0 g (3.5 mmol) of the ketone **3b** in 50 ml of 1:1 benzene–ether. The mixture was stirred under reflux for <1.5 hr. and was then hydrolyzed with 10% NH_4Cl solution (200 ml). The organic layer was separated, washed with water and Na_2CO_3, and dried ($MgSO_4$). Evaporation of the ether left a red oil which was taken up in methanol (30 ml) containing 2 drops of 12 M HCl and heated under reflux for 12 h. Removal of the methanol gave a yellow oil (2.0 g) which was freed from traces of acid and was then chromatographed on alumina (50 g) using hexane as the eluent. A colorless oil (0.2 g) was obtained which solidified after 5 days to white prisms (0.2 g, 19%), mp 119.5–120 °C. Recrystallization from hexane followed by sublimation gave an analytical sample: mp 119–120 °C; NMR ($CDCl_3$) δ 7.3–7.7 (m, 6 H, aromatic), 6.95 (s, 1 H, aromatic C_5H), 4.6 (2 H, quartet, 2 H), 4.0 (s, 3 H, OCH_3), 1.93 (s, 3 H, CH_3), 1.85 (s, 3 H, CH_3). The AB quartet centered at 4.6 has J_{AB} = 16 Hz and δ_{AB} = 34 Hz. Anal. Calcd for $C_{20}H_{18}OS$: C, 78.39; H, 5.92; S, 10.47. Found: C, 78.46; H, 6.06; S, 10.22.

Registry No.—**3b**, 59463-61-5; **5**, 59463-62-6; **6**, 59463-63-7; **7**, 59463-64-8; **8**, 59463-65-9; **9**, 59463-66-0; **10**, 59463-67-1; **11**, 59463-68-2; 2,3-dibromothiophene, 3140-93-0; 2-methoxynaphthaldehyde, 5392-12-1; isopropyl bromide, 75-26-3.

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A Reaction of Chlorosulfonyl Isocyanate and 6-Tritylaminopenicillanic Acid Leading to the Anhydropenicillin Rearrangement

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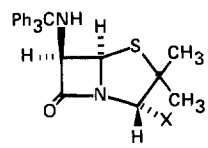
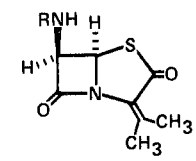
Received April 12, 1976

Since their initial preparation,[1] anhydropenicillins have continued to attract interest.[2] We now report a reaction of 6-tritylaminopenicillanic acid (1) with chlorosulfonyl isocyanate (CSI) that leads to the formation of anhydro-6-tritylaminopenicillanic acid (**5**).





1, X = COOH
2, X = CN
3, X = $CO_2CONHSO_2Cl$
4, X = $CONHSO_2Cl$

5, R = $-CPh_3$
6, R = $-H$, $CH_3(C_6H_4)SO_3H$

In connection with other work, we attempted a synthesis of the penicillin nitrile **2** from carboxylic acid **1** by application of the methods of Lohaus[3] and Vorbrüggen.[4] These involve, respectively, treatment of a chlorosulfonylamide with either an amide such as dimethylformamide (DMF, Scheme I) or a base such as triethylamine (Scheme II). In favorable cases, the chlorosulfonylamide is readily obtained by reacting a carboxylic acid with CSI.

When **1** was treated with a 5% molar excess of CSI in acetonitrile, followed by either DMF or triethylamine, no β-lactam containing materials were isolated with the neutral fraction. Various speculations may be proposed to account for the failure of these straightforward approaches patterened after the successful conditions of Lohaus and Vorbrüggen. The β-lactam moiety perhaps interacted with the chlorosulfonylamide **4**[3,5] or it reacted directly with the CSI.[5] The possibility of other undesirable reactions involving CSI and compounds **1**, **2**, **3**, or **4** may also be inferred.[5] Finally, the fact that penicillins are relatively strong acids[6] may have hampered the $CO_2H \rightarrow CN$ conversion because, according to results of both Lohaus and Vorbrüggen, the CSI reaction is sluggish with strong acids.

On the assumption that the β-lactam amide was the major cause of our difficulties, we treated **1** with CSI in the presence of either DMF or triethylamine. Neither small nor large amounts of DMF were useful, likely because the rate of CSI reaction with DMF[5] was faster than that with the penicillin carboxyl group. When, however, triethylamine was present during the CSI addition, we isolated[7] a fairly pure penicillin derivative contaminated by some triphenylcarbinol[8] according to ir, NMR, and TLC analysis. The presence of two vinylic methyl group resonances suggested that the anhydropenicillin rearrangement had occurred to afford anhydro-6-tritylami-