autoclaved dent field corn kernels at 28 °C and separated from substrate and other fungal material by using general procedures that have been previously described.[3] Sclerotial samples were stored at 4 °C until extraction. Proton and carbon NMR data were obtained in $CDCl_3$ on a Bruker WM-360 spectrometer, and chemical shifts were recorded by using the signal for the residual protiated solvent (7.24 ppm) as a reference. Carbon multiplicities were established by a DEPT experiment. One-bond C–H correlations were obtained by using an XHCORR pulse sequence optimized for 135 Hz. Proton signals studied with the selective INEPT technique were individually subjected to four separate experiments, optimizing for 4, 7, 10, or 15 Hz. HREIMS data were obtained on a VG ZAB-HF mass spectrometer, and the low-resolution spectrum was obtained on a VG TRIO 1 quadrupole instrument. Details of other experimental procedures and insect bioassays have been described elsewhere.[3-5,16]

Isolation and Properties of Tubingensin A. Sclerotia of *A. tubingensis* (500–750-μm diameter, 98.7 g) were produced by using 360 g of autoclaved corn kernels as substrate. The harvested sclerotia were ground with a mortar and pestle and triturated repeatedly with hexane (10 × 100 mL). The combined hexane extracts were filtered and evaporated to afford 474 mg of a yellow oil. This residue was subjected to crude preliminary separation by reversed-phase semipreparative HPLC (5-μm C_{18} column; 250 × 10 mm; 90:10 MeOH–H_2O at 2.0 mL/min). Fractions containing tubingensin A were rechromatographed on the same column at 85:15 MeOH:H_2O to afford 20 mg of tubingensin A (**3**) as a light yellow solid: mp 95–98 °C; HPLC retention time 17.7 min (90:10 MeOH–H_2O); $[\alpha]_D$ 13.6° (*c* 1.0, $CHCl_3$); UV (MeOH) 340 (ε 480), 326 (480), 302 (6780), 262 (6930), 239 (18 200), 218 nm (14 900); ^1H NMR and ^{13}C NMR, see Table I; EIMS (30 eV) 401 (M^+, rel intensity 38%), 318 (100), 300 (52), 260 (11), 246 (40), 234 (21), 232 (25), 220 (28), 206 (51), 180 (32), 146 (10), 130 (5); HREIMS, obsd 401.2698, calcd for $C_{28}H_{35}NO$ 401.2720.

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(16) Dowd, P. F. *Entomol. Exp. Appl.* **1988**, *47*, 69.

Thioanhydrides. 3. Synthesis, Properties, and Diels–Alder Reactions of Sulfur Analogues of 1,8-Naphthalic Anhydride†,[1]

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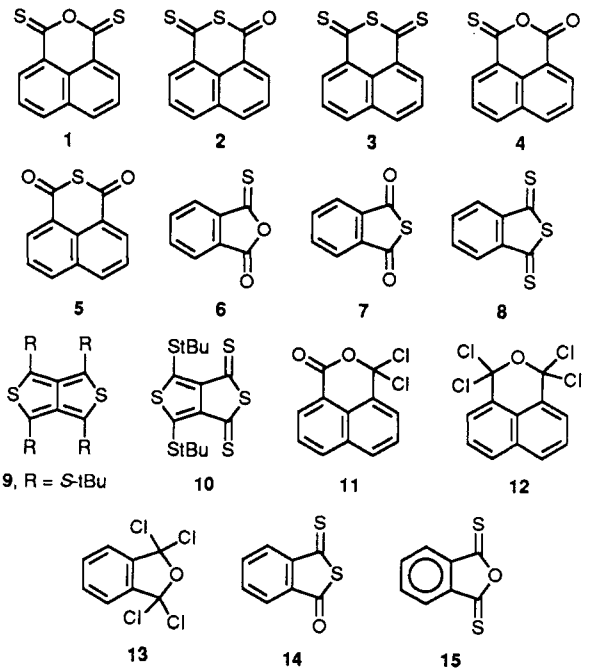
All five possible sulfur analogues of 1,8-naphthalic anhydride have been synthesized by practical procedures, starting from 1,8-naphthalic anhydride. The thionoanhydrides containing an oxygen bridge rearrange readily to thiolo isomers under tertiary amine catalysis, and all of the thionoanhydrides undergo (4 + 2) cycloadditions with norbornylene. In addition, other α-thiono-substituted naphthalenes have been probed in the norbornylene addition reaction, and some observations have been made concerning the mechanism of the Pedersen thionation reaction.

In contrast to the extensive chemistry of cyclic carboxylic anhydrides, very little is known concerning thiocarbonyl analogues containing either five-membered or six-membered rings.

In the five-membered series, thionophthalic anhydride **6** was obtained unexpectedly in 1967 from the reaction of phthaloyl chloride and hydrogen disulfide; it was quite unstable thermally and isomerized readily to the thiolo-anhydride **7**.[2] The rather more stable thionothiolophthalic anhydride **14** was reported by us in 1988 by an interesting reaction discussed in more detail below.[3] Trithiophthalic anhydride (**8**) has not yet been described, although the thiophene derivative **10**, which represents the first five-membered trithioanhydride, was reported in 1986 as a remarkable oxidation product of the stable thieno[3,4-*c*]-thiophene derivative **9**.[4]

The first six-membered thionoanhydrides (**1–3**), belonging to the 1,8-naphthalic anhydride series, were reported by us briefly in 1984.[5] We now present synthetic details of this work, as well as the synthesis of the remaining two sulfur analogues (**4** and **5**) of 1,8-naphthalic anhydrides, some mechanistic studies on the Pedersen thionation, and some expanded observations on the Diels–Alder addition of norbornylene to α-thiono-substituted naphthalenes.



Results and Discussion

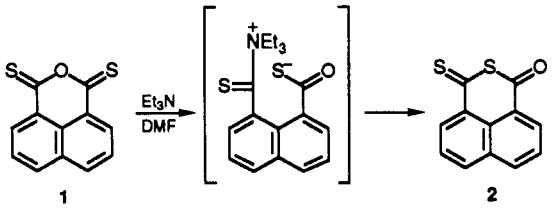
Synthesis of the Five Possible 1,8-Naphthalic Thioanhydrides. Our initial thionation study involved the acid chloride of 1,8-naphthalic acid. This compound has been known for some time, but there was ambiguity

† For Part 2, see ref 3.

(1) A preliminary account of this work was presented in a plenary lecture by M. P. Cava at the 13th International Conference on Organic Sulfur Chemistry, held at Odense, Denmark, in August 1988.

0022-3263/89/1954-4746$01.50/0

Scheme I



concerning its formulation as a normal acid chloride or a pseudo acid chloride.[6] The asymmetry of its NMR spectrum now clearly indicates that it must be assigned the pseudo acid chloride structure **11**. Reaction of **11** with Lawesson's reagent (LR) in refluxing chlorobenzene afforded beautiful red needles of the dithiono anhydride **1**.[5] Later, it was found that direct thionation of 1,8-naphthalic anhydride also furnished **1**, albeit much more slowly and in somewhat lower yield. The latter synthesis is actually the most practical if carefully defined experimental conditions are employed.

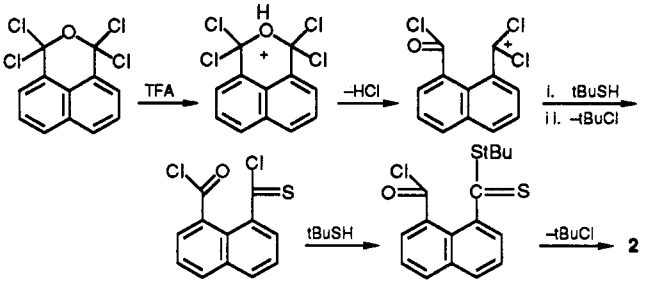
The red dithione **1** rearranged rapidly in the presence of a catalytic amount of triethylamine in cold DMF to give the isomeric green thionothioloanhydride **2**. Our proposed mechanism for this rearrangement, which does not occur in the absence of the base, is shown in Scheme I. A ring-opened betaine is initially generated, which recyclizes by attack of the more nucleophilic sulfur of the monothiocarboxylate ion.

In contrast to the dithione **1**, the carbonyl-containing green isomer **2** reacted rapidly (30 min) with LR in boiling chlorobenzene to give the very stable trithioanhydride **3** as black iridescent needles, the structure of which was confirmed by X-ray crystallography.[5]

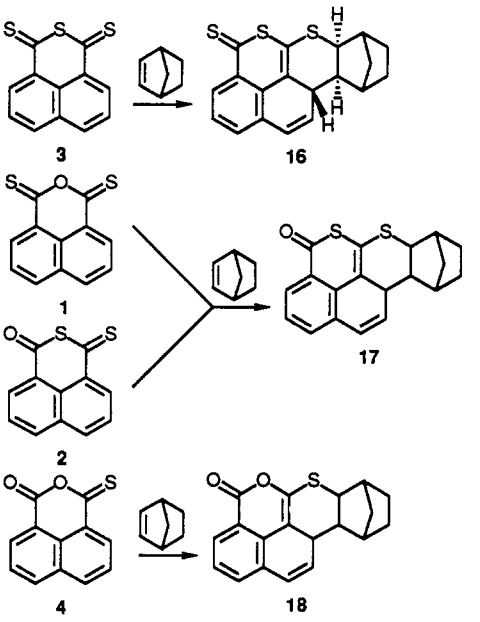
In 1931, Szperl described the synthesis of a monothio derivative of 1,8-naphthalic anhydride by the action of hydrogen sulfide on naphthaloyl chloride.[7] Repetition of this reaction has afforded a homogeneous, orange-red crystalline product, to which we have assigned the monothionoanhydride structure **4** on the basis of its asymmetric NMR spectrum (see the Experimental Section). As in the case of dithione **1**, monothione **4** is rearranged cleanly by triethylamine. The resulting yellow thioloanhydride **5** could not be prepared from 1,8-naphthalic anhydride by the usual Reissert synthesis, viz. reaction with sodium sulfide followed by acidification. Surprisingly, tri-*n*-butylphosphine also caused the rearrangement of **4** to **5**, rather than an expected desulfurization. On the other hand, **4** was recovered unchanged when heated for several hours with the less nucleophilic triphenyl phosphine.

Studies on the Pedersen Thionation Reaction. Some time ago, Pedersen et al. found that several readily solvolyzed *gem*-dihalides (i.e., benzophenone dichloride) were converted to thiocarbonyl compounds upon treatment with *tert*-butylmercaptan and trifluoroacetic acid.[8] We reported recently that 1,1,3,3-tetrachloro-1,3-dihydroisobenzofuran (**13**) was converted into thionothiolophthalic anhydride (**14**) under these conditions and speculated that the unknown dithionophthalic anhydride (**15**) might be a transient intermediate in this reaction.[3] We decided to probe the mechanism of this reaction further by extending it to the 1,8-naphthalic series, where all of the thioanhydrides were now available. The tetrachloronaphthopyran (**12**) corresponding to **13** was easily prepared from 1,8-naphthalic anhydride by exhaustive treatment with phosphorus pentachloride. Tetrachloride **12** underwent a rapid Pedersen reaction to give, in good yield, the green thionothioloanhydride **2**; none of the dithione isomer **1** was obtained. The dithione **1** was not an intermediate in this reaction, since it was completely unchanged by *tert*-butylmercaptan and trifluoroacetic acid. A plausible mechanism for the formation of **2** from chloride **12** is shown in Scheme II.

Scheme II



Scheme III

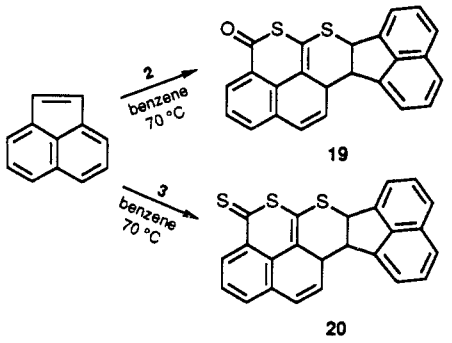


The pseudo chloride **11** also undergoes the Pedersen reaction readily with the formation of thionoanhydride **4**. In this case, halide solvolysis should occur without ring opening, which would generate a high-energy acylium ion.

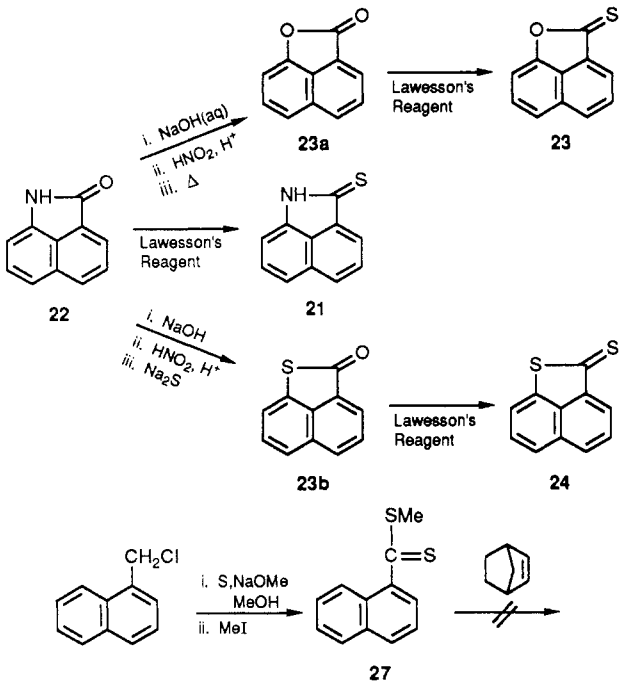
Diels–Alder Reactions. The trithioanhydride was found to undergo a nonphotochemical addition to norbornylene under remarkably mild conditions. The resulting bright red adduct was shown to have structure **16** by X-ray crystallography.[5] The formation of this adduct may be viewed as involving an inverse demand (2 + 4) cycloaddition of the norbornylene olefinic bond to an electron-deficient ene–thione moiety of the aromatic thioanhydride system. Some analogy to this reaction may be found in the addition of norbornylene to the α-dithione function of the dimethyl tetrathiooxalate.[9]

(2) Sharts, C. M.; Fong, D. W. *J. Org. Chem.* **1967**, *32*, 3709.
(3) Raasch, M. S.; Huang, N. Z.; Lakshmikantham, M. V.; Cava, M. P. *J. Org. Chem.* **1988**, *53*, 891.
(4) Yoneda, S.; Ozaki, K.; Yanagi, K.; Minobe, J. *J. Chem. Soc., Chem. Commun.* **1986**, 19.
(5) Lakshmikantham, M. V.; Carroll, P.; Furst, G.; Levinson, M. I.; Cava, M. P. *J. Am. Chem. Soc.* **1984**, *106*, 6084.
(6) (a) Mason, F. A. *J. Chem. Soc.* **1925**, *125*, 2116. (b) Davies, W.; Leeper, G. W. *J. Chem. Soc.* **1927**, 1124. (c) Arient, J.; Marhen, J. *Collect. Czech. Chem. Commun.* **1963**, *28*, 1292.
(7) Szperl, L. *Rocz. Chem.* **1930**, *10*, 652; *Chem. Abstr.* **1931**, *25*, 938.
(8) Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223.

Scheme IV



Scheme V

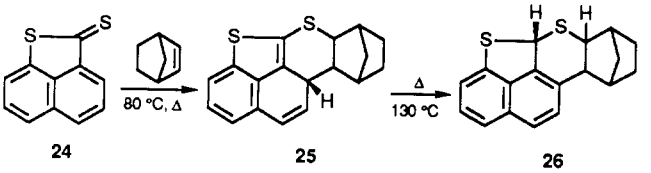


Similar Diels–Alder additions were observed when norbornylene was heated with any of the other three thiononaphthalic anhydrides (**1**, **2**, or **4**), but not with the thioloanhydride **5**. Unexpectedly, dithione **1** gave the same carbonyl-containing adducts as monothione **2**, albeit more slowly. Since **1** does not rearrange to **2** under the same conditions in the absence of norbornylene, the olefin would appear to be catalyzing the isomerization of **1** to **2** prior to cycloaddition. The nature of this isomerization process is not clear at this time (see Scheme III).

Thionoanhydrides **2** and **3** also reacted with acenaphthylene to give adducts **19** and **20**, respectively, indicating that strained electron-rich alkenes other than norbornylene can function as dienophiles with these thiones (see Scheme IV).

Several *peri*-substituted naphthalenes (**21**, **23**, **24**) containing a thiocarbonyl function in a five-membered ring were prepared in order to ascertain their propensity to give Diels–Alder adducts with norbornylene. Thiolactam **21** was obtained by direct thionation of naphthostyril (**22**). Thionolactone **23** and dithiolactone **24** were prepared in several steps from naphthostyril as indicated in Scheme V. In this series, only dithiolactone **24** afforded an adduct (**25**) with norbornylene. Adduct **25** underwent a 1,3-hydrogen shift on heating in chlorobenzene at 130 °C for 3 h to give the naphthalene isomer **26** (Scheme V). In contrast to this behavior, adduct **16** was recovered unchanged upon heating for prolonged periods of time.

Scheme VI



Methyl α-dithionaphthoate (**27**),[10] although formally an acyclic analogue of **24**, did not react with norbornylene (Scheme VI). Its unreactivity may be attributed to the *peri* effect of the C-8 hydrogen, which should prevent the thiocarbonyl group from assuming a conformation in which it is coplanar to the naphthalene ring.

Experimental Section

General Procedures. All NMR spectra were run in $CDCl_3$ solution, chemical shifts are reported in δ units downfield from TMS, and J values are in hertz. Infrared spectra were determined on KBr mulls, and bands are expressed in frequency units ($\nu^{cm^{-1}}$).

1,8-Naphthaloyl Chloride (11). This was prepared according to ref 6a. Its NMR spectrum was unsymmetrical: δ 8.48 (dd, 1 H, J = 7.5, 2.5), 8.26 (dd, 1 H, J = 7.5, 2.5), 8.19 (d, 1 H, J = 7.5), 8.06 (d, 1 H, J = 7.5), 7.73 (t, 2 H, J = 7.5).

Tetrachloronaphthopyran (12). To an intimate mixture of 1,8-naphthalic anhydride (39.6 g) and phosphorus pentachloride (85 g) was added phosphorus oxychloride (50 mL) (fume hood). The mixture was heated at 160 °C (oil bath temperature) for 3.5 days, protected from moisture. The resulting clear brown liquid was subjected to distillation under water pump vacuum, taking care to introduce a drying tower ($CaCl_2$) between the suction pump and the receiver. Phosphorus oxychloride distilled over at 78 °C (bath temperature) at ~30 mm pressure. When the rate of distillation slowed down, dry toluene (50 mL) was added to the reaction flask to chase $POCl_3$. After distillation of 2 × 50 mL toluene, the resulting brown oil was cooled and treated with hexane (50 mL) containing CH_2Cl_2 (15 mL) and allowed to stand at room temperature for some time; the resulting white crystals were isolated by decantation and washed with dry hexane to give 38 g of crude **12** (62%). The crude material was crystallized once from boiling hexane containing CH_2Cl_2 (180:30) to yield white needles: mp 125–132 °C (29 g; 47% yield); NMR δ 8.13 (dd, 2 H, J = 8.1, 1.0 Hz), 8.00 (dd, 2 H, J = 8.5, 1.0), 7.68 (t, 2 H, J = 8.0, 8.4); mass spectrum, m/e 306 (M^+, 3.1), (271, M – Cl, 100). The compound was prone to partial hydrolysis upon exposure to air. It was used without further purification.

Dithiono-1,8-naphthalic Anhydride (1). Method A. 1,8-Naphthaloyl chloride (**11**) (7.2 g) and Lawesson's reagent[11] (17.3 g) in chlorobenzene (140 mL) were heated under reflux for 3 h. The dark brown solution was evaporated under reduced pressure, the residue was heated with absolute ethanol, and the dark red solid was filtered and dried (2.6 g). Crystallization from boiling chlorobenzene furnished pure dithionoanhydride **1**: mp 212 °C dec; 2.0 g (30%); NMR δ 8.83 (d, 2 H, J = 8.0 Hz), 8.28 (d, 2 H, J = 7.5 Hz), 7.8 (t, 2 H, J = 8.0, 7.5 Hz); mass spectrum, m/e 230 (M^+, 100), 202 (80), 186 (50), 170 (60), 126 (60); IR 1214, 1138, 834, 761 cm^{-1}. Anal. Calcd for $C_{12}H_6OS_2$: C, 62.62; H, 2.63; S, 27.80. Found: C, 62.34; H, 2.56; S, 28.03.

Method B. To a boiling solution of 1,8-naphthalic anhydride (16.0 g) in chlorobenzene (350 mL) was added Lawesson's reagent[11] (32.0 g) in portions, in the course of 1.5 h. The mixture was refluxed for 9 h more. The brick red solid obtained by cooling was filtered. The solid was boiled with ethanol (300 mL), filtered, and dried to give 7.2 g crude dithiononaphthalic anhydride. Two

(9) Hartke, K.; Kissel, T.; Quante, J.; Henssen, G. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 953.

(10) Schönberg, A.; Nickel, S.; Cernik, D. *Ber.* **1932**, *65*, 289.

(11) Thomsen, I.; Clausen, K.; Scheibye, S.; Lawesson, S. O. *Org. Synth.* **1984**, *62*, 158.

recrystallizations from chlorobenzene furnished long silky red needles of pure **1**, 4.5 g (24% yield), identical with a sample prepared via method A.

Thiolothiono-1,8-naphthalic Anhydride (2). Method A. Dithionoanhydride **1** (3.1 g) was suspended in DMF (125 mL) and treated with five drops of Et_3N. The red suspension turned into a green solution. After 10 min, water (50 mL) was added, and the dull green precipitate was filtered; it was washed with water and dried to give 2.0 g crude product. The filtrate furnished 1 g more product. Crystallization of the combined solid from CH_2Cl_2–hexane yielded 2.2 g of **2** as olive green needles (71%): mp 210 °C dec; NMR δ 9.01 (dd, 1 H, J = 7.5, 1.0), 8.59 (dd, 1 H, J = 7.5, 1.0), 8.32 (dd, 1 H, J = 7.5, 1.0), 8.28 (dd, 1 H, J = 7.50, 1.0), 7.76 (t, 1 H, J = 7.5, 1.0), 7.72 (t, 1 H, J = 7.50, 1.0); mass spectrum, m/e 230 (M^+, 100), 202 (64.1), 186 (39.8), 170 (35.7), 158 (25.0), 126 (58.8); IR 1640 (CO), 1250 (C=S) cm^{-1}. Anal. Calcd for $C_{12}H_6OS_2$: C, 62.62; H, 2.63; S, 27.80. Found: C, 62.39; H, 2.72; S, 27.91.

Method B. A mixture of tetrachloride **12** (2.6 g) and tBuSH (2.6 mL) in CH_2Cl_2 (25 mL) (protected from moisture) was treated with trifluoroacetic acid (0.2 mL). The evolution of HCl became brisk within 5 min, and the thionothiolonaphthalic anhydride **2** crystallized out of the solution. After gas evolution ceased, the practically pure product was filtered (fume hood) and washed with methanol and dried. The yield was 1.48 g (75%) of thiolothionoanhydride, identical in all respects with a sample prepared by method A.

Action of tBuSH and TFA on Dithiono-1,8-naphthalic Anhydride. A suspension of dithiononaphthalic anhydride (**1**) (110 mg) in CH_2Cl_2 (5 mL) was treated with tBuSH (0.1 mL) and TFA (0.1 mL). The mixture was left aside at room temperature for several days. Workup led to the recovery of starting material (100 mg).

Trithio-1,8-naphthalic Anhydride (3). A mixture of thionothioloanhydride **2** (8.8 g) and Lawesson's reagent (8.0 g) in chlorobenzene (160 mL) was refluxed for a half hour. Upon cooling, heavy iridescent crystals of **3** separated. These were filtered, washed with cold chlorobenzene and ethanol successively, and dried to give practically pure **3** (8.1 g; 80%): mp 225 °C; NMR δ 8.89 (dd, 2 H, J = 7.65, 1.1), 8.28 (dd, 2 H, J = 8.1, 1.3), 7.69 (t, 2 H, J = 7.85, 7.88); mass spectrum, m/e 246 (M^+, 100), 214 (49.9), 202 (37), 170 (37), 126 (59). An analytical sample was made by recrystallization from chlorobenzene. Anal. Calcd for $C_{12}H_6S_3$: C, 58.55; H, 2.46; S, 38.99. Found: C, 58.55; H, 2.43; S, 39.02.

Monothiono-1,8-naphthalic Anhydride (4). Method A. 1,8-Naphthaloyl chloride (**11**) (2.5 g) in CH_2Cl_2 (20 mL) was treated with tBuSH (1.8 g) and a drop of TFA. Within minutes there was copious evolution of HCl, and the product separated as coppery red plates. After 1.5 h, the insoluble precipitate was filtered (fume hood) and washed with methylene chloride and ethanol successively to give practically pure **4** (1.8 g; 84%): mp >210 °C dec; NMR δ 8.89 (dd, 1 H, J = 7.76, 1.0), 8.62 (dd, 1 H, J = 7.31, 1.0), 8.30 (d, 2 H, J = 8.28), 7.883–7.741 (m, 2 H); mass spectrum, m/e 214 (M^+, 96.8), 186 (76.3), 158 (15.0), 154 (67.7), 126 (100). An analytical sample was prepared by recrystallization from chlorobenzene, and the melting point did not change. Anal. Calcd for $C_{12}H_6O_2S$: C, 67.28; H, 2.82; S, 14.96. Found: C, 67.07; H, 2.76; S, 14.83.

Method B. 1,8-Naphthaloyl chloride (**11**, 0.63 g) was dissolved in dry toluene (8 mL). Hydrogen sulfide was bubbled through the solution, which was warmed to 40 °C. The reaction was over in minutes, and the product separated as orange-red crystals. It was filtered, washed, and dried to yield pure **4** (0.43 g, 81% yield), identical in all respects with a sample prepared as above.

Thiolo-1,8-naphthalic Anhydride (5). A suspension of thionoanhydride **4** (100 mg) in boiling methylene chloride (5 mL) was treated with triethylamine (0.1 mL). The resulting yellow precipitate was filtered, washed successively with water and methanol, and dried to yield **5** (70 mg). Crystallization from chlorobenzene furnished pure **5**: mp >230 °C dec; NMR δ 8.65 (dd, 2 H, J = 7.42, 1.3), 8.32 (dd, 2 H, J = 8.2, 1.15), 7.79 (tr, 2 H, J = 7.74, 7.85); mass spectrum, m/e 214 (M^+, 73.1), 186 (70.7), 154 (69.2), 126 (100); IR 1640 cm^{-1}. Anal. Calcd for $C_{12}H_6O_2S$: C, 67.28; H, 2.82; S, 14.96. Found: C, 67.21; H, 2.85; S, 14.87.

Attempted Desulfurization of 4. A mixture of thionoanhydride **4** (50 mg) and tri-*n*-butylphosphine (0.2 mL) in chlorobenzene (5 mL) was boiled for 15 min. The red color lightened, and upon cooling, yellow crystals of **5** separated. These were filtered, washed with methanol, and dried (40 mg).

Adduct 16 from 3. A mixture of trithioanhydride **3** (0.24 g) and norbornylene (0.14 g) in benzene (10 mL) was heated on the steam bath gently for a half hour. The solvent was evaporated, and the residue was crystallized from ethanol–methylene chloride to give the bright red adduct **16** (0.25 g): mp 170 °C; NMR δ 8.803 (m, 1 H), 7.05 (m, 2 H), 6.70 (m, 1 H), 6.40 (m, 1 H), 3.15 (m, 1 H), 2.70 (br, 1 H), 2.60 (m, 1 H), 2.35 (m, 1 H), 2.20 (m, 1 H), 1.6–1.8 (m, 3 H), 1.1–1.4 (m, 3 H). Anal. Calcd for $C_{19}H_{16}S_3$: C, 67.05; H, 4.74; S, 28.21. Found: C, 67.11; H, 4.71; S, 28.16.

Adduct 17 from 2. Reaction of **2** (150 mg) and norbornylene (170 mg) in boiling benzene (3 mL) was over in 10 min. The solvent was evaporated, and the residue was crystallized from ethanol–methylene chloride to give yellow crystals of **17** (170 mg, 80%): mp 150 °C; NMR δ 8.17 (dd, 1 H, J = 5.75, 3.61), 7.43 (m, 2 H), 6.67 (dd, 1 H, J = 10.25, 1.55), 6.42 (dd, 1 H, J = 10.25, 3.95), 3.23 (m, 1 H), 2.84 (m, 2 H), 2.45 (m, 2 H), 1.86 (m, 2 H), 1.43 (m, 3 H); mass spectrum, m/e 324 (M^+, 38), 230 (100), 202 (31); IR 3200, 2990, 1750, 1650, 1450, 1250, 1040, 900, 830, 740 cm^{-1}. Anal. Calcd for $C_{19}H_{16}OS_2$: C, 70.34; H, 4.97; S, 19.76. Found: C, 70.01; H, 5.01; S, 19.61.

Adduct 17 from 1. A mixture of **1** (0.3 g) and norbornylene (0.37 g) in benzene (30 mL) was refluxed for 6 h. After cooling, evaporation followed by chromatography of the residue (SiO_2/hexane–EtOAc, 8:1) yielded yellow crystals (0.2 g, 50%), identical in all respects with **17**, prepared from **2**.

Adduct 18 from 4. Thionoanhydride **4** (0.3 g) and norbornylene (0.34 g) were mixed in benzene and refluxed. Within 20 min a yellow solution resulted. After 2 h of refluxing, the mixture was cooled, and the resulting pale yellow crystals of adduct **18** were filtered. Recrystallization from ethyl acetate–hexane afforded pure **18** (0.35 g, 82% yield): mp 161 °C; NMR δ 8.05 (dd, 1 H, J = 7.29, 1.80), 7.42 (m, 2 H), 6.65 (dd, 1 H, J = 10.02, 1.90), 6.34 (dd, 1 H, J = 10.02, 3.68), 3.0 (m, 1 H), 2.93 (m, 1 H), 2.73 (s, 1 H), 2.42 (s, 1 H), 2.21 (d, 1 H, J = 10.00), 1.87 (m, 3 H), 1.43 (m, 3 H); mass spectrum, m/e 308 (M^+, 84), 214 (100), 186 (56), 154 (12); IR 2970, 2900, 1735, 1640, 1620, 1600, 1480, 1150, 820, 770 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_2S$: C, 74.01; H, 5.23; S, 10.42. Found: C, 74.21; H, 5.11; S, 10.16.

Adduct 20 from 3 and Acenaphthylene. A mixture of **3** (0.61 g) and acenaphthylene (0.38 g) in benzene (40 mL) was refluxed for 2 h. Upon cooling, adduct **27** crystallized out. Recrystallization from chlorobenzene gave red crystals, which were very insoluble in ordinary solvents. Adduct **27** had mp > 250 °C: IR 1430, 1250, 1100, 980, 820, 790 cm^{-1}. Anal. Calcd for $C_{24}H_{14}S_3$: C, 72.36; H, 3.51; S, 24.12. Found: C, 72.21; H, 3.48; S, 24.02.

Adduct 19 from 2 and Acenaphthylene. Reaction of **2** (0.5 g) and acenaphthylene (0.33 g) in refluxing benzene for 3 h furnished adduct **26** after standard workup. It formed pale yellow crystals (0.64 g, 78% yield): mp 198 °C; NMR δ 7.98 (m, 1 H), 7.66 (m, 6 H), 7.36 (m, 2 H), 6.98 (dd, 1 H, J = 10.32, 1.9), 6.68 (dd, 1 H, J 10.32, 4.02), 5.26 (d, 1 H, J = 8.28), 4.89 (m, 1 H), 4.17 (m, 1 H); IR 3300, 1650, 1590, 1530, 1450, 900, 820, 810, 780, 690 cm^{-1}. Anal. Calcd for $C_{24}H_{14}OS_2$: C, 75.36; H, 3.69; S, 16.76. Found: C, 74.97; H, 3.61; S, 16.61.

Thiolactam 21. A mixture of naphthostyril[12] (1.69 g) and Lawesson's reagent (2.43 g) in toluene (35 mL) was refluxed for 4 h. The solvent was removed in vacuo, and the residue was filtered through silica using benzene–hexane (2:1) eluant. Crystallization from methylene chloride–hexane gave crystals of **19** (1.52 g; 82.1% yield): mp 156 °C dec; NMR δ 9.76 (br s, 1 H, NH), 8.26 (d, 1 H, J = 7.2), 8.11 (d, 1 H, J = 8.08), 7.52 (m, 4 H); mass spectrum, m/e 185 (M^+, 100), 127 (M^+ – 58, 18.7). Anal. Calcd for $C_{11}H_7NS$: C, 71.35; H, 3.78; N, 7.56; S, 17.29. Found: C, 71.17; H, 3.82; N, 7.50; S, 17.20.

Thionolactone 23. A mixture of lactone **23a**[13] (0.34 g, 40 mL) and Lawesson's reagent (0.675 g) in chlorobenzene was heated at 125 °C for 6 h. The solvent was removed under reduced pressure, and the residue was chromatographed on silica gel, employing benzene–hexane (1:2) as eluent, to give an orange solid. Recrystallization from methylene chloride–hexane gave large

(12) Bamberger, E.; Philip, M. *Ber.* **1887**, *20*, 237.
(13) Ekstrand, A. G. *Ber.* **1886**, *19*, 1131.

crystals of **20** (0.28 g, 75%): mp 142 °C dec; mass spectrum, *m/e* 186 (M^+, 60.8). Anal. Calcd for $C_{11}H_6OS$: C, 70.96; H, 3.22; S, 17.2. Found: C, 70.84; H, 3.29; S, 17.13.

Dithiolactone 24. A mixture of thioloactone **23b**[14] (1.2 g) and Lawesson's reagent (1.4 g) in chlorobenzene (15 mL) was heated for 4 h at 120 °C. The solvent was removed in vacuo, and the residue was chromatographed on silica gel, eluting with ethyl acetate–hexane (1:8) to give 1.1 g (85%) of dark reddish crystalline dithiolactone **24**: mp 98 °C dec (lit.[14] mp 96–97 °C); mass spectrum, *m/e* 202 (M^+, 100), 158 (M^+ – 44, 35.2).

Adduct 25 from 24 and Norbornylene. A mixture of dithiolactone **24** (0.5 g) and norbornylene (0.69 g) in benzene (14 mL) was refluxed for 10 h under N_2. The solvent was removed, and the residue was chromatographed on silica with benzene–hexane (1:4) to give 0.45 g (61%) of adduct **24**: mp 114 °C; NMR δ 7.56 (d, 1 H, *J* = 8.06), 7.25 (m, 1 H), 7.04 (d, 1 H, *J* = 7.3), 6.7 (d, 1 H, *J* = 9.82), 6.27 (d, 1 H, *J* = 9.81), 3.16 (m, 1 H), 2.83 (m, 1 H), 2.64 (br, 1 H), 2.34 (m, 1 H), 2.23 (m, 1 H), 1.9–1.7 (m, 3 H), 1.2–1.4 (m, 3 H); mass spectrum, *m/e* 296 (M^+, 4.2), 202 (M^+ – 94, 100). Anal. Calcd for $C_{18}H_{16}S_2$: C, 72.97; H, 5.4; S, 21.62. Found: C, 72.94; H, 5.46; S, 21.55.

Thermal Isomerization of Adduct 24 to 25. A solution of cycloadduct **24** (0.32 g) in chlorobenzene (10 mL) was heated for 3 h at 130 °C under N_2. The residue, after removal of chlorobenzene, was chromatographed on silica, employing methylene chloride–hexane (1:4) to give a white solid. Crystallization from methylene chloride–hexane gave white crystals of **25** (0.19 g, 60%): mp 185 °C; NMR δ 7.64 (d, 1 H, *J* = 8.48), 7.52 (d, 1 H, *J* = 8.42), 7.43 (m, 1 H), 7.34 (m, 1 H), 7.20 (m, 1 H), 5.78 (s, 1 H), 3.65 (m, 1 H), 2.94 (br, 1 H), 2.75 (m, 1 H), 2.35 (m, 1 H), 1.9–1.7 (m, 2 H), 1.6–1.3 (m, 3 H), 1.15 (m, 1 H); mass spectrum, *m/e* 296 (M^+, 26.3), 202 (M^+ – 94, 100). Anal. Calcd for $C_{18}H_{16}S_2$: C, 72.97; H, 5.4; S, 21.62. Found: C, 72.40; H, 5.41; S, 21.40.

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(14) Nakayama, J.; Dan, S.; Hoshino, M. *J. Chem. Soc., Perkin Trans. 1* **1981**, 413.

Synthesis of α-Phosphono Lactones and Esters through a Vinyl Phosphate–Phosphonate Rearrangement

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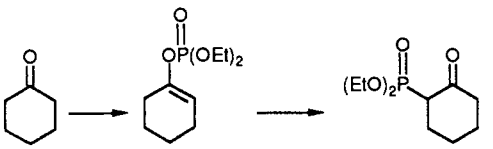
Upon treatment with base, the diethyl vinyl phosphate derivatives of five-, six-, and seven-membered-ring lactones undergo rearrangement to α-phosphono lactones in very good yields. Because the vinyl phosphates can be prepared in situ, these α-phosphono lactones can be obtained from the parent lactones in a one-flask protocol, making this methodology a convenient alternative to the traditional Arbuzov synthesis. An analogous reaction sequence can be used to prepare some α-phosphono esters, but yields are generally lower and the rearrangement becomes minimal with esters hindered at the β-position.

We recently introduced a new and general route to cyclic β-keto phosphonates, which is based upon the rearrangement of a vinyl phosphate anion to a β-keto phosphonate anion (Scheme I).[2] To continue probing the limits of this rearrangement, and to extend its utility, we turned our attention to its potential application in the synthesis of α-phosphono lactones.[3] While some α-phosphono lactones have been prepared from the analogous α-bromo compounds through the Arbuzov approach,[4] few α-bromo lactones are commercially available. Accordingly, preparation of α-phosphono lactones by a route based on a vinyl phosphate to phosphonate rearrangement would be attractive, particularly if a one-flask protocol from the lactone to its phosphonate derivative could be established. In this report, the results of this approach to α-phosphono lactones are presented, along with our efforts to prepare α-phosphono esters by an analogous reaction sequence.

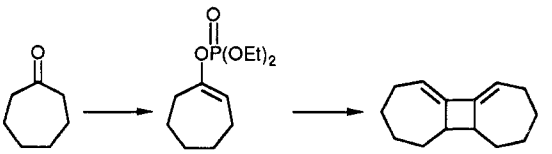
Results and Discussion

Because dialkyl vinyl phosphate derivatives of cyclic ketones rearrange readily to β-keto phosphonates upon

Scheme I



Scheme II



treatment with LDA,[2] the vinyl phosphate derivatives of lactones might be expected to react under similar conditions. The required vinyl phosphates can be obtained by sequential treatment of a lactone with LDA and a dialkyl phosphorochloridate. However, ^{31}P analysis of these reactions indicated mixtures more complex than expected. When HMPA was added to the reaction mixture, the desired vinyl phosphates were obtained cleanly,[5a] and either *N,N'*-dimethyl-*N,N'*-propyleneurea (DMPU)[5b] or 12-

(1) Fellow of the Alfred P. Sloan Foundation, 1985–1989.

(2) (a) Hammond, G. B.; Calogeropoulou, T.; Wiemer, D. F. *Tetrahedron Lett.* **1986**, *27*, 4265. (b) Calogeropoulou, T.; Hammond, G. B.; Wiemer, D. F. *J. Org. Chem.* **1987**, *52*, 4185.

(3) Portions of this work were reported at the 196th American Chemical Society Meeting, Los Angeles, CA, Sept 1988.

(4) Buchel, K. H.; Rochling, H.; Korte, F. *Justus Liebigs Ann. Chem.* **1965**, *685*, 10.

(5) (a) Charbonnier, F.; Moyano, A.; Greene, A. E. *J. Org. Chem.* **1987**, *52*, 2303. (b) Mukhopadhyay, T.; Seebach, D. *Helv. Chim. Acta* **1982**, *65*, 385.

0022-3263/89/1954-4750$01.50/0