83.67; H, 8.89. Found: C, 83.59; H, 8.79.

Use of 2,4,5,6,6-pentamethyl-3-methyl-d_3-2,4-cyclohexadienone (**4**-d_3)[9] in place of **4** gave **5**-d_6 as white needles, mp 331 °C dec, whose ^{1}H NMR spectrum differed from that of **5** in that the peak at δ 1.69 was absent and the peak at δ 1.78 sharpened to a singlet. Therefore, these peaks can be assigned to the C3, C7 and C2,C6 methyls, respectively: mass spectrum (CI), *m/e* (relative intensity) 436 (91), 435 (100), 364 (19), 295 (7), 281 (8); high-resolution mass spectrum calcd for $C_{30}H_{32}D_6O_2$ 436.32483, found 436.32471.

Use of 2,4,6,6-tetramethyl-3,5-dimethyl-d_6-2,4-cyclohexadienone (**4**-d_6)[9] in place of **4** gave **5**-d_{12} as white needles, mp 327 °C dec, whose ^{1}H NMR spectrum differed from that of **5** in that the peaks at δ 1.69 and 1.62 were absent and the peak at δ 1.78 sharpened to a singlet. Therefore, the peak at δ 1.62 can be assigned to the C1,C5 methyls and the peak at δ 1.67 is due to the C4,C8 methyls: mass spectrum, *m/e* (relative intensity) 442 (M^+, trace), 372 (M^+ - dimethylketene, 8), 302 (M^+ - 2 - dimethylketene, 100), 70 (29); high-resolution mass spectrum calcd for $C_{30}H_{26}D_{12}O_2$ 442.36249, found 442.36263.

Acid-Catalyzed Rearrangement of 5. A solution of **5** (500 mg, 1.16 mmol) in 50 mL of neat TFA was heated at reflux for 21 h, then cooled, and poured into ice-water. The mixture was extracted with methylene chloride (3 × 100 mL), and the combined extracts were washed with saturated aqueous $NaHCO_3$ (3 × 50 mL), dried ($MgSO_4$), and evaporated to dryness. The crude product mixture was chromatographed on a preparative silica gel plate with 4:1 chloroform-hexane (five developments) to afford 207.5 mg (41.5%) of **13**, mp 256-257 °C, 90 mg (18%) of **14**, mp 248-249 °C, 69.5 mg (14%) of **15**, mp 313-314 °C, and 38 mg (8%) of **16**, mp 335-336 °C. NMR integration of the aromatic proton region (δ 6.7-8) in the crude product before chromatography gave the yields shown in eq 5. Samples for all spectra were obtained by recrystallization from ethanol. For the ^{1}H and ^{13}C NMR spectra of **13**-**16**, see Table I. For **13**: mass spectrum, *m/e* (relative intensity) 430 (23), 415 (100), 387 (4), 360 (3), 345 (5), 237 (3), 179 (3), 165 (4); IR (KBr) 2970, 2930, 2887, 1655, 1600, 1430, 1380, 1280, 1213, 1195 cm^{-1}; UV ($CHCl_3$) λ_{max} 246 nm (ϵ 2700); high-resolution mass spectrum, calcd for $C_{30}H_{38}O_2$ 430.28716, found 430.28717. for **14**: mass spectrum, *m/e* (relative intensity) 430 (28), 415 (100), 360 (16), 330 (4), 275 (6), 149 (28); IR (KBr) 2968, 2930, 1720, 1670, 1598, 1450, 1380, 1260, 1210 cm^{-1}; high-resolution mass spectrum found 430.28701. For **15**: mass spectrum, *m/e* (relative intensity) 430 (17), 415 (100), 385 (1), 200 (22); IR (KBr) 2986, 2930, 2875, 1670, 1440, 1400, 1376, 1272, 1185, 1158 cm^{-1}; UV ($CDCl_3$) λ_{max} 239 nm (ϵ 2100); high-resolution mass spectrum found 430.28717. For **16**: mass spectrum, *m/e* (relative intensity) 430 (100), 415 (78), 387 (18), 361 (10), 265 (7), 251 (3), 97 (84); IR (KBr) 3010, 2985, 2930, 2875, 1650, 1615, 1385, 1320, 1305, 1228 cm^{-1}; UV ($CHCl_3$) λ_{max} 240 nm (ϵ 2200); high-resolution mass spectrum found 430.28749.

Deuteriation of 13 and 16. The diketone (15 mg) was dissolved in 20 mL of methanol-*d* containing 0.1 g of sodium and heated at reflux for 30 h. The cooled solution was added to 100 mL of methylene chloride and washed with water (2 × 25 mL). Any residual base was neutralized with solid CO_2. Removal of the solvent in vacuo gave 14 mg (93%) of deuteriated diketone. For the ^{1}H NMR spectra of **13**-d_3 and **16**-d_6, see the text. Neither **14** nor **15** underwent exchange under these conditions.

Irradiation of 16. A degassed solution of **16** (20 mg) in 20 mL of spectroscopic grade acetone was irradiated for 21 h by using a 450-w Hanovia lamp with a Pyrex filter. Removal of the solvent in vacuo gave essentially pure **17**, contaminated with <2% of **16**. for **17**: mp 367 °C dec; ^{1}H NMR δ 6.89 (s, 2 H), 1.48 (s, 6 H), 1.28 (s, 6 H), 1.19 (s, 6 H), 1.14 (s, 6 H), 0.96 (s, 6 H), 0.34 (s, 6 H); ^{13}C NMR δ 199.03, 136.87, 136.12, 117.59, 54.70, 45.32, 42.07, 39.96, 35.97, 23.00, 17.65, 13.13, 9.96, 7.83, 5.60; mass spectrum, *m/e* (relative intensity) 430 (100), 415 (84), 387 (16), 361 (12), 333 (11), 303 (10), 275 (8), 245 (9), 205 (3), 97 (57); IR (KBr) 2975, 2921, 1715, 1460, 1387, 1323, 1270, 1048, 985 cm^{-1}; high resolution mass spectrum calcd for $C_{30}H_{38}O_2$ 430.28716, found 430.28701.

X-ray Data for 5. Cell dimensions: a = 7.942 (3) Å, b = 16.715 (6) Å, c = 9.234 (2) Å, β = 96.38 (2)°; V = 1218.2 (6) Å^3, ρ = 1.17 g/cm^3; $C_{30}H_{38}O_2$, FW 430.64, Z = 2; monoclinic $P2_1/n$; Mo Kα (λ = 0.71073 Å; 2406 reflections total, 2153 unique; Nicolet P3F diffractometer, direct methods, full-matrix least-squares refinement, R = 0.041.

Acknowledgment. We thank the National Institutes of Health (GM 15997) for financial support of this research. We thank Dr. Donald L. Ward for carrying out the X-ray structure determination on **5**.

Supplementary Material Available: Tables of positional parameters, thermal parameters, bond distances, bond angles, and torsional angles for the crystal structure of **5** (12 pages). Ordering information is given on any current masthead page.

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Benzothiet-2-ones: Synthesis, Reactions, and Comparison with Benzoxet-2-ones and Benzazetin-2-ones

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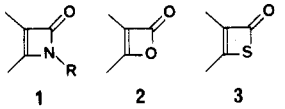
Benzothiet-2-one (**5**) is obtained as a neat solid, stable below -20 °C (-45 °C in solution), by flash vacuum pyrolysis of benzothiophene-2,3-dione (**9**). Naphtho[2,3-*b*]thiet-2-one (**21**) and naphtho[2,1-*b*]thiet-1-one (**42**) are obtained as stable crystalline solids in near-quantitative yields from the corresponding napthothiophenediones **20** and **41**. Naphtho[2,3-*b*]oxet-2-one (**31**) and naphtho[2,3-*b*]azetin-2-one (**36**) were generated and observed by IR spectroscopy to be stable below -40 °C and 0 °C, respectively. The thietones, oxetones, and azetinones undergo rapid ring-opening reactions with methanol to give the corresponding carboxylic acid esters. They undergo thermal CO elimination with concomitant Wolff-type ring contraction to thioketenes (**17**, **25**, **45**), ketenes (**30**), and nitriles (**37**), respectively. The di-, oligo-, and polymerization of the thietones has been elucidated. Naphtho[2,1-*b*]thiet-1-one (**42**) reacts with 1-thiocarbonyl-1*H*-indene (**45**) to give cycloaddition product **46**. Naphthothietones **21** and **42** react with dicyclohexylcarbodiimide to furnish 2-imino-1,3-thiazin-4-one derivatives **47** and **49**.

The four-membered unsaturated heterocycles **1**-**3** are little-known and generally highly reactive compounds.



1 **2** **3**

Unsubstituted azetinones (**1**, R = H) can only be isolated at low temperatures,[2,3] but phenyl and bulky alkyl sub-

(1) Present address: Hoechst AG, Frankfurt, West Germany.

(2) (a) Ziegler, E., Sterk, H. *Monatsh. Chem.* **1968**, *99*, 1958. (b) de Champlain, P.; Luche, J.-L.; Marty, R. A.; de Mayo, P. *Can. J. Chem.* **1976**, *54*, 3749-3756.

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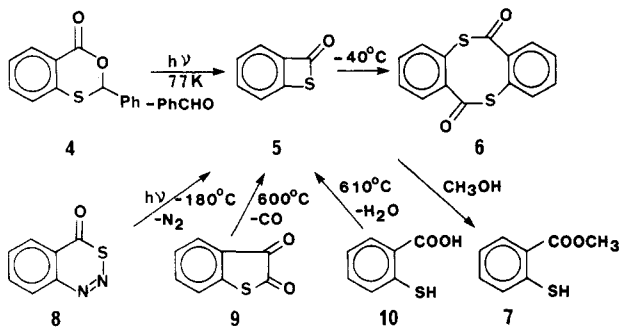
Scheme I



stituents R stabilize the compounds sufficiently to permit the isolation of annelated derivatives at room temperature.[4-7]

In the oxygen series (**2**), benzoxet-2-one has been matrix isolated at 8 K and observed by infrared spectroscopy ($\nu_{C=O}$ 1904 cm^{-1}).[8] A claim to the preparation of naphtho[2,3-*b*]oxet-2-one as a stable crystalline compound[9] will be refuted below. Likewise, the compound described as 1-phenylpyrazol[3,4-*b*]oxetone by Stanovnik et al.[10] has been found not to possess that structure.[11]

In the sulfur series (**3**) no stable thietone has been prepared prior to this work. Chapman and McIntosh obtained benzothietone (**5**) by photolysis of 2-phenyl-3,1-benzoxathian-4-one (**4**) at 77 K.[12] **5** was observed by IR spectroscopy ($\nu_{C=O}$ 1803 cm^{-1}) and dimerized at −40 °C to **6**. Trapping with methanol gave the methyl ester **7**.[12] In subsequent work, the carbonyl absorption at 1803 cm^{-1} was also observed by IR spectroscopy at −180 °C following irradiation of the thiadiazine **8**.[13] The photoelectron spectrum of **5** was obtained by gas-phase pyrolysis of both benzothiophene-2,3-dione (**9**) and 2-mercaptobenzoic acid (**10**).[14]

The only monocyclic thietone prepared so far is 3-benzoyl-4-phenylthiet-2-one.[15] Although this compound is unstable above −40 °C, a full infrared, NMR, and mass spectral characterization has been achieved.[15]

We now report the synthesis of the naphthothietones **21** and **42** as stable, crystalline compounds.[16] Because of the successful preparation of these compounds, we have also reinvestigated the synthesis of benzothietone (**5**) and

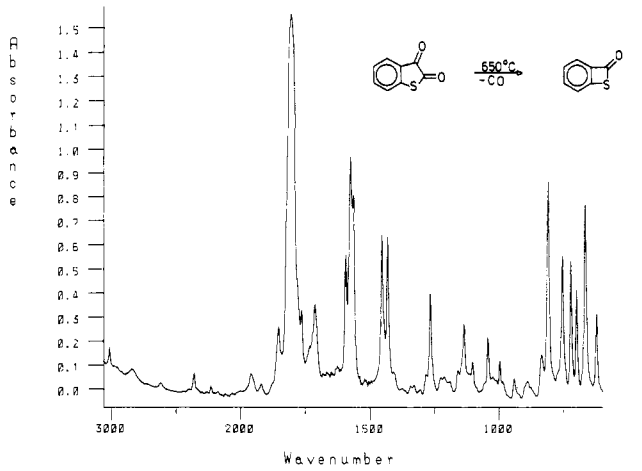
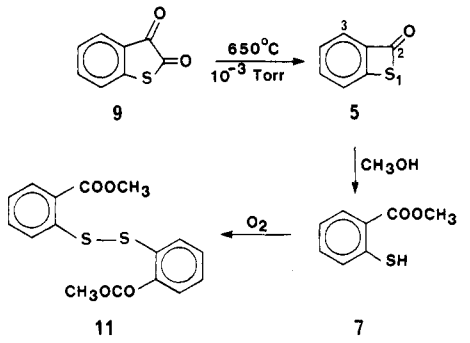


Figure 1. FT-IR spectrum of benzothiet-2-one at −196 °C.

Scheme II



find that this material can be obtained as a neat solid or in solution below −40 °C.

Results and Discussion

Benzothiet-2-one. Benzothietone (**5**) is obtained in nearly quantitative yield (94%) as a pale-yellow solid by flash vacuum pyrolysis (FVP) of benzothiophene-2,3-dione (**9**) at 650 °C. The product is isolated on a cold finger cooled with liquid nitrogen. It is stable to ca. −20 °C in the solid state, at which temperature rapid polymerization as well as partial di- and trimerization takes place (see below). When kept in a vacuum at −20 °C, benzothietone sublimes in large part before it oligomerizes.

The IR spectrum of **5** (Figure 1) is obtained by condensing the material on a KBr window at 77 K. The strong carbonyl absorption at 1800 cm^{-1} is particularly characteristic. The slight difference from the band position reported by Chapman[12] may be due to the presence of benzaldehyde in the latter case.[12] The remaining absorption bands of benzothietone (see Experimental Section) are in good agreement with the band positions previously noted in the photolysis of **4**.[12]

The ^1H and ^{13}C NMR spectra of **5** are obtained by condensing $CDCl_3$ onto the solid thietone at 77 K. Gentle warming allows the solution to drip into a cooled NMR tube. The sample should be kept below −45 °C at all times as otherwise di-, tri- and polymerization take place. In the ^{13}C NMR, the carbonyl group appears at 175.4 ppm and the quaternary carbons at 144.8 and 143.7 ppm. The remaining signals and the couplings observed are typical of an ortho-disubstituted benzene derivative (see Experimental Section).

Benzothietone reacts below −40 °C with methanol to give methyl *o*-mercaptobenzoate (**7**) in 85% isolated yield. Small amounts of the dimer and trimer as well as the

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(4) Ege, G.; Beisiegel, E. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 303.
(5) (a) Olofson, R. A.; Vander Meer, R. K.; Stournas, S. *J. Am. Chem. Soc.* **1971**, *93*, 1543. (b) Olofson, R. A.; Morrison, D. S.; Banerji, A. *J. Org. Chem.* **1984**, *49*, 2652. (c) Olofson, R. A.; Vander Meer, R. K.; Hoskin, D. H.; Bernheim, M. Y.; Stournas, S.; Morrison, D. G. *Ibid.* **1984**, *49*, 3367–3372. (d) Olofson, R. A.; Vander Meer, R. K. *Ibid.* **1984**, *49*, 3377–3379.
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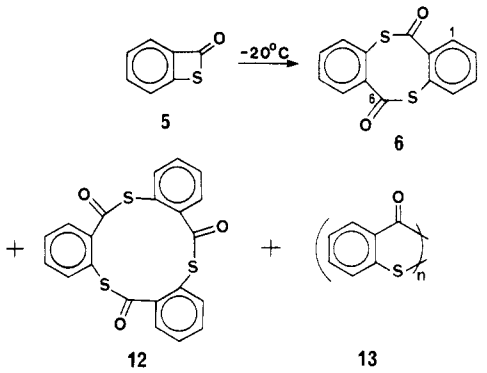
(13) Fanning, A. T., Jr.; Bickford, G. R.; Roberts, T. D. *J. Am. Chem. Soc.* **1972**, *94*, 8505–8509.
(14) (a) Schulz, R.; Schweig, A. *Tetrahedron Lett.* **1979**, 59–62. (b) For thermolysis of **9** to **6** in liquid paraffin, see: Tsuge, O.; Tashiro, M.; Kanemasa, S.; Takasaki, K. *Chem. Lett.* **1972**, 828.
(15) Wentrup, C.; Winter, H.-W.; Gross, G., Netsch, K.-P.; Kollenz, G.; Ott, W.; Biedermann, A. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 800.
(16) A preliminary account of part of this work is given in ref 3.

Scheme III



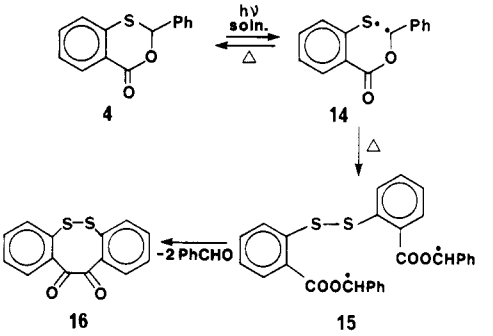
disulfide **11** (8%) are also obtained under these conditions. The thiol **7** is completely oxidized to the disulfide **11** by prolonged stirring in the presence of air (Scheme II). This observation confirms the suggested mechanism of formation of the diethyl ester corresponding to **11** on photolysis of **4** in the presence of ethanol[17] and of the dibutyl ester corresponding to **11** on thermolysis of **8** in the presence of butanol.[13]

The di- and polymerization of benzothietone have been the subject of some controversy. Pedersen et al.[17] found that the photolysis of **4** in chloroform or hydrocarbon solution gave the dimer **16** in near-quantitative yield. Chapman,[12] however, reported that the dimer of **5** was the dithiosalicylide **6**. Roberts et al.[13] isolated **6** in 23% yield from the thermal decomposition of thiadiazolone **8** at 174 °C. A yellow residue, presumably polymeric, was not examined. All authors[12,13,17] based their assignments of the structures of the dimer on direct comparison with an authentic sample of **6** prepared according to the method of Baker et al.[18] The structure of authentic dithiosalicylide **6** has been confirmed by X-ray crystallography.[19]

We find that benzothietone (**5**) does not just dimerize: it dimerizes, trimerizes, and polymerizes, and the polymer is by far the major product. The trimer and the polymer both have strong IR bands near 900 cm^{-1}, but the dimer does not; instead the dimer has a double band at 920 and 930 cm^{-1}. Since Chapman[12] based his observation of the formation of the *dimer* **6** on the appearance of a strong band at 900 cm^{-1}, we conclude that he, too, in fact obtained trimer and/or polymer as the major products.

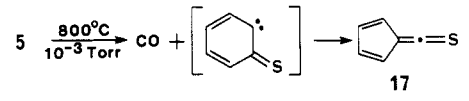
When solid benzothietone (**5**) is warmed to ca. −20 °C, exothermic polymerization sets in (see Scheme III). If the layer of **5** is sufficiently thick (e.g., 500 mg), the liberated heat suffices to partially melt and vaporize the sample. The product is an opaque, brown, glassy, and very hard mass. The dimer **6** (13–29%) and trimer **12** (6–15%) were separated by thick layer chromatography and identified by comparison of TLC behavior, IR, ^1H NMR, ^{13}C NMR, and mass spectra with those of authentic samples prepared according to Baker et al.[18] The tetramer[18] was not detectable in the oligomerization of **5**. The polymer (**13**), which accounts for the remaining 56–81% of the product, has IR, ^1H NMR, and ^{13}C NMR spectra very similar to those of the tetramer, but the ^1H NMR signals are significantly broadened. The polymer is soluble in $CDCl_3$ and the solubility reaches a maximum at 42 °C. Both heating and cooling of this solution causes precipitation. After filtering and drying the polymer, it can be largely redissolved in $CDCl_3$, from which solution it then slowly precipitates once more at room temperature. Multiple repetition of this exercise finally produces a hard, insoluble polymeric material.

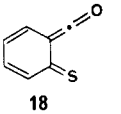
Scheme IV



The dimer isolated by Pedersen et al.[17] from the solution photolysis of **4** obviously has spectral characteristics and TLC behavior different from those of **6**. Furthermore, this dimer is formed in quantitative yield in $CHCl_3$ and hydrocarbon solution, and there is no indication that **6**, **12**, or **13** is formed at all. Pedersen's dimer cannot, therefore, be derived from benzothietone (**5**). A plausible mechanism for the formation of the Pedersen dimer **16** is set out in Scheme IV. The starting material **4** undergoes thermally reversible homolysis to the diradical **14**.[17] *In solution*, this diradical may dimerize to **15** prior to the expulsion of benzaldehyde. With a preformed *S–S* bond, the dimer **16** will result. This reaction pathway is not available for the neat benzothietone under the experimental conditions used by Chapman[12] and ourselves. It was only in ethanol solution that Pedersen et al.[17] obtained the diethyl ester corresponding to **11** (28% yield), together with "large amounts of polymer" and only a trace of dimer **16**. Since the nature of their polymer was not examined, it is impossible at present to decide whether benzothietone (**5**) was involved in the experiments of Pedersen et al. at all.

FVP of benzothiophenedione **9** or of benzothietone (**5**) at 800 °C causes loss of CO from **5** and a Wolff-type ring contraction to thiocarbonylcyclopentadiene (**17**). While **17** has been observed by gas-phase photoelectron spectroscopy,[14] it was too unstable for direct detection in another FVP study of benzothiadiazole.[20] We observed the IR absorption of the thioketene in **17** at 1709 cm^{-1} by condensation of the pyrolysis product on a BaF_2 window at 77 K. When the product is condensed at 15 K, carbon monoxide is observed as well (2137 cm^{-1}) and identified by comparison with literature values[21] and by the fact that it evaporates from the surface at ca. 54 K. No infrared evidence for ketene **18**, a possible valence tautomer of **5**,[17] could be found under any conditions.





(17) Pedersen, A. O.; Lawesson, S.-O.; Klemmensen, P. D.; Kolc, J. *Tetrahedron* **1970**, *26*, 1157–1161.
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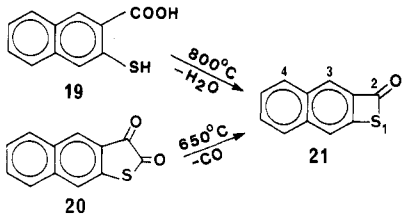
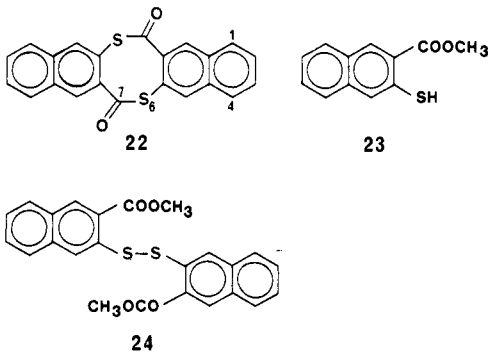
Scheme V



Naphtho[2,3-*b*]thiet-2-one, -oxet-2-one, and -azet-in-2-one. The naphthothietones are stable, crystalline solids at room temperature. In our first experiments, naphtho[2,3-*b*]thietone (**21**) was obtained in 20% yield by FVP of 3-mercaptonaphthalene-2-carboxylic acid (**19**). A better yield (95%) is obtained by pyrolysis of the thiophenedione **20** (Scheme V). **21** has been fully characterized by its spectral data and elemental analysis (see Experimental Section). In the crystalline state, **21** is stable for days at room temperature and permanently at −18 °C. In solution, di-, oligo-, and polymers are formed within minutes. The dimer **22** was isolated in 10% yield following heating of solid **21** to its melting point (ca. 85 °C); still lower yields of dimer are obtained from solutions of **21** in various nonhydroxylic solvents, the major product being an intractable polymer. In contrast, hydroxylic solvents such as methanol cause rapid and quantitative conversion of **21** to the methyl ester **23**. As in the benzene series, **23** is extremely sensitive to atmospheric oxygen and oxidized to the disulfide **24** in 90% in the course of 12 h in chloroform solution.

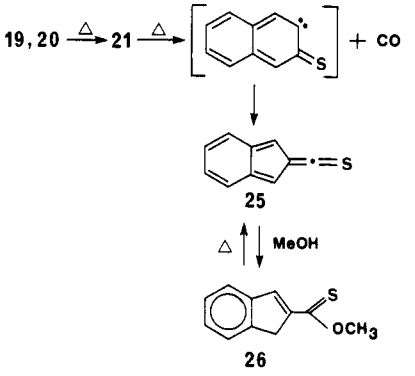


The FVP of either **19** or **20** at 900 °C causes complete disappearance of the thietone **21**. Instead, a new compound absorbing weakly at 1742 cm^{-1} is observed by IR spectroscopy (−196 °C). This compound is stable below −100 °C and disappears on warming between −100 and −80 °C as observed by IR spectroscopy. When the pyrolysis products are isolated in Ar matrix at 15 K, the byproduct CO can be observed as well (2137 cm^{-1}). Co-condensation of the pyrolysis products with methanol followed by warm-up to −120 °C causes disappearance of the 1742 cm^{-1} band and formation of the ester **26**, which was isolated and identified by direct comparison with an authentic sample prepared by reaction of methyl indene-2-carboxylate with Lawesson's reagent.

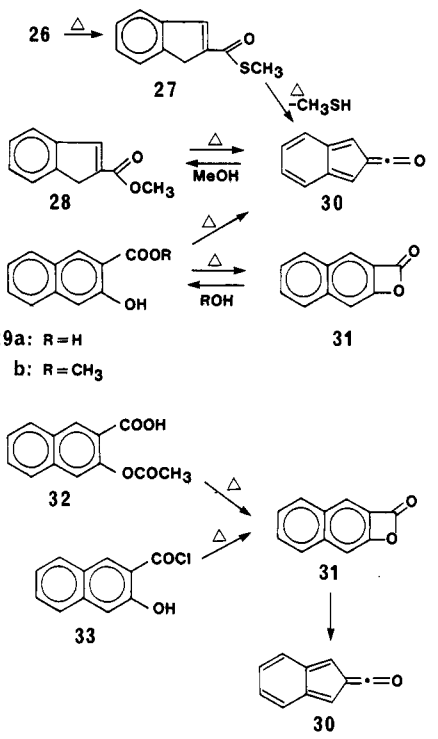
The 1742 cm^{-1} band is therefore assigned to the isoindenoid thioketene **25** (Scheme VI).

Pyrolysis of **26** at 800 °C partly regenerates **25**, which can again be observed by IR monitoring of the 1742 cm^{-1} band at −196 °C. However, in this latter pyrolysis, a ketene is formed as well, absorbing strongly at 2127 cm^{-1} in the IR. This ketene we interpret as 2-carbonyl-2*H*-indene (**30**), whose formation requires a methyl group shift in **26** to give the *S*-methyl ester **27** prior to loss of methanethiol (Scheme VII). Confirmation of this interpretation is given by the

Scheme VI



Scheme VII

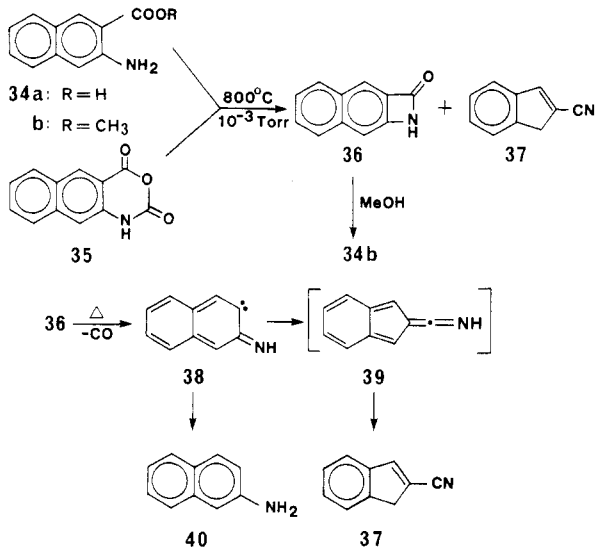


observation that the same ketene is formed by pyrolysis of **28**, **29a,b**, **32**, and **33**, as indicated in Scheme VII. In each case, the same 2127 cm^{-1} band was recorded at low temperature, and in each case warm-up in the presence of methanol caused disappearance of the ketene (at ca. −120 °C) and formation of the ester **28**. The formation of ketene **30** by pyrolysis of **29b** as well as **28** has already been demonstrated by mass spectrometry in the work of Grützmacher and Hübner.[22] The present work, in conjunction with that of Grützmacher and Hübner,[22] solidly establishes the structure of ketene **30**.

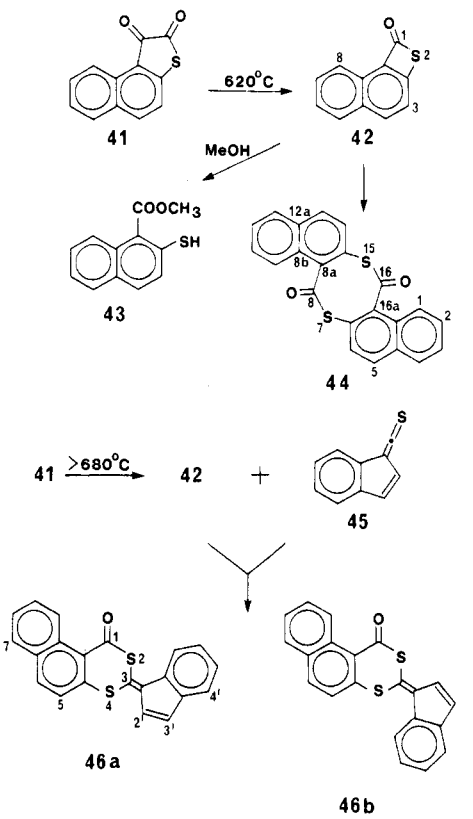
There was no indication in the previous work[22] of the formation of any other compound, except that of indene in the pyrolysis of ester **28**. We find, however, that the pyrolyses of **29a,b 32**, and **33** at 750 °C/10^{-3} Torr all give rise to a new major product that absorbs strongly at 1893 and 1874 cm^{-1} in the IR (−196 °C) and is stable below −40 °C. We ascribe these new bands to the oxetone **31** because, when the compound is generated in the presence of methanol, it can still be observed by IR spectroscopy at −196 °C, but warming to −40 °C causes disappearance of the carbonyl bands and formation of the ester **29b**. Low-

(22) Grützmacher, H. F.; Hübner, J. *Liebigs Ann. Chem.* **1973**, *793*–798.

Scheme VIII



Scheme IX



ering of the pyrolysis temperature (700–750 °C) causes an increase in the intensities of the carbonyl bands at 1893 and 1874 cm^{-1} relative to that of the ketene **30** at 2127 cm^{-1}. Increasing the pyrolysis temperature (800–900 °C) causes disappearance of **31** and an increase in the intensity of the ketene band of **30**.

Naphtho[2,3-*b*]oxet-2-one (**31**) has been reported previously as a stable, crystalline compound.[9] We have repeated this preparation and find that the product is polymeric. The comparison between oxetone **31** and thietone **21** demonstrates that oxetones are far less stable than the corresponding thietones, and all reports of the isolation of unhindered oxetones at room temperature should be treated with scepticism.[9,10,23]

For further comparison, naphtho[2,3-*b*]azetin-2-one (**36**) was also generated from three different precursors (**34a,b** and **35**; Scheme VIII). In each case, the azetone was observed at 1778 cm^{-1} and found to be stable on warm-up to 0 °C. Reaction with methanol gave the ester **34b** in 20% isolated yield. A further signal at 2215 cm^{-1} in these pyrolyses is due to 2-cyanoindene (**37**), which was isolated and identified by comparison with an authentic sample from other work.[24] The likely mechanism of formation of **37** involves loss of CO from the azetone **36** to give imino carbene **38** (Scheme VIII). The same carbene (**38**) has previously been generated by FVP of naphtho[2,3-*b*]triazole and found to undergo ring contraction to **37**, presumably via a Wolff-type rearrangement leading first to ketenimine **39**.[24] In agreement with the earlier work,[24] 2-cyanoindene (**37**) interconverts with 3-cyanoindene via reversible 1,5-sigmatropic shifts of H and CN at temperatures above 800 °C, and at 1000 °C isomerization to 4(7)- and 5(6)-cyanoindenes is observed as well.[24] In the FVP of **34a** at 800 °C, an 8% yield of 2-naphthylamine (**40**) was also isolated, thus lending further support to the imino carbene intermediate **38**. Hydrogen abstractions of this type have been previously observed for other imino carbene intermediates generated from triazoloarenes and isatins.[24,25] Similar results were also obtained in the pyrolysis of methyl anthranilate to benzazet-2-one and cyanocyclopentadiene,[2b] of 3-aminopyridine-2-carboxylic acid to azeto[3,2-*b*]pyridin-2(1*H*)-one and 2-cyanopyrrole, and of 3-aminopyridine-4-carboxylic acid to azeto[2,3-*c*]pyridin-2(1*H*)-one.[3]

From the results obtained for the three isosteric compounds **21**, **31**, and **36**, the following order of stabilities is derived: thietones > azetones > oxetones.

Naphtho[2,1-*b*]thiet-1-one (42). This compound is obtained as bright orange crystals in virtually quantitative yield by FVP of the corresponding thiophenedione **41** at 620 °C (Scheme IX). **42** does not possess a well-defined melting point since polymerization takes place above ca. +40 °C. The compound is permanently stable at −18 °C, and at room temperature it is transformed into a mixture of dimer, trimer, and polymer in the course of several days. The same takes place in nonhydroxylic solvents within minutes. A 20% yield of the dimer **44** was isolated after heating solid **42** to 40 °C. Dissolution of **42** in methanol affords the ester **43** quantitatively, and as in the case of the isomer **23**, ester **43** is readily oxidized to the corresponding disulfide in air.

FVP of **41** at 900 °C causes disappearance of the thietone and formation of the thioketene **45** (1739 cm^{-1}), which on warm-up is stable to −40 °C, at which temperature it polymerizes. The formation of the thioketene **45** starts at a pyrolysis temperature of 680 °C. The same product is also formed together with unreacted thietone **42** by FVP of **42** itself at 750 °C. At this temperature, the product consists of approximately equal amounts of **42** and **45**. Warm-up of the mixture of **42** and **45** from −196 °C causes disappearance of both compounds at ca. −50 °C as monitored by IR spectroscopy. At the same time, a new compound is formed, which can be isolated in 70% yield at room temperature. On the basis of the elemental and mass spectral analyses and the ^1H and ^{13}C NMR spectra, the new compound is identified as benzofulvene derivative **46**, formed by reaction of the thietone **42** with the thioketene **45** (Scheme IX). The chemical shifts and coupling constants observed in the ^1H and ^{13}C NMR spectra are typical of a 1,2-substituted naphthalene as well as an ortho-di-

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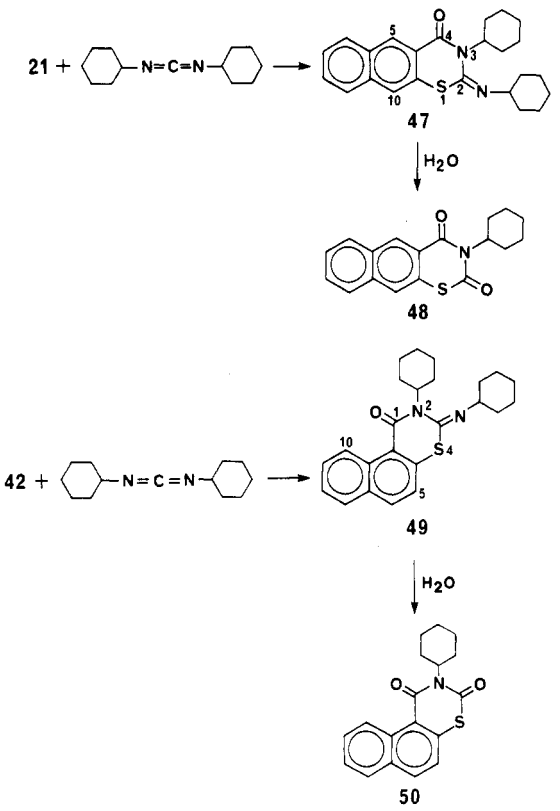
(24) Wentrup, C.; Crow, W. D. *Tetrahedron* **1970**, *26*, 3965–3981.
(25) Wentrup, C. *Helv. Chim. Acta* **1972**, *55*, 1613–1617.

Scheme X



substituted benzene derivative. Two further vinylic hydrogens as well as two vinylic and two quaternary carbons are indicative of the annelated fulvene system.[26] The two vinylic protons appear as doublets δ 7.03 and 6.96 (^3J = 5.5 Hz) in the ^{1}H NMR spectrum with positions and couplings similar to those found for other benzofulvene derivatives.[27] While both structures **46a** and **46b** are possible for this compound, steric considerations suggest that **46a** is more likely. We have found no spectroscopic evidence for a ring opening of thietone **42** to a thioketo ketene isomer (cf. **18**). Because of this, and because the reaction between **42** and **45** takes place already at −50 °C, it is likely initiated by a direct nucleophilic attack of the S atom of the thioketene on the carbonyl group of the thietone, and/or attack of the S atom of the thietone on the central C atom of the thioketene.

Cycloaddition Reactions. The reaction between **42** and **45**, described in Scheme IX above, suggests that thietones might undergo formal cycloaddition chemistry with other dienophiles. For example, nitriles, isocyanates, and carbodiimides have been used to trap keto ketenes.[28] Benzothiete has been reported to undergo cycloaddition reactions with dimethyl acetylenedicarboxylate, *N*-phenylmaleimide, and methyl acrylate.[29] Olofson reported a cycloaddition reaction between *N-tert*-butylbenzazete and phenyl isocyanate.[5d]

We find, however, that thietones are very reluctant to undergo such formal cycloaddition. No reaction was observed between **21** and dimethyl acetylenedicarboxyate, 4-phenyl-3,5-dihydro-1,2,4(4*H*)-triazole-3,5-dione, benzonitrile, acetonitrile, or phenyl isocyanate.

In contrast, both **21** and **42** undergo smooth reaction with dicyclohexylcarbodiimide at 60 °C, giving the adducts **47** and **49**, respectively (Scheme X).

47 and **49** can be hydrolyzed to the thiazinediones **48** and **50**, respectively. For proof of structure, a sample of **48** was also prepared by treatment of **19** with dicyclohexylcarbodiimide and subsequent hydrolysis according to a procedure previously applied to *o*-mercaptobenzoic acid.[30]

Conclusion. The naphthothietones are stable, crystalline compounds, highly reactive toward nucleophiles, and easily polymerizable. Benzothietone is stable below ca. −40 °C. Addition reactions with carbodiimides (Scheme X) and thioketene (Scheme IX) indicate that relatively nucleophilic cycloaddition partners are required. No evidence for valence tautomerization to thiocarbonyl ketenes of type **18** as a prelude to cycloaddition chemistry has been found. Comparison of the thietones with azetones and oxetones demonstrates decreasing (kinetic) stability in that series. Thietones, azetones, and oxetones all undergo thermal CO extrusion with ensuing Wolff-type ring contraction to thioketenes, nitriles, and ketenes, respectively.

Experimental Section

General Methods. The pyrolysis equipment was as previously described.[31] In preparative pyrolyses the products were isolated on cold fingers cooled with liquid N_2. For spectroscopic observation of unstable products, these were condensed on salt windows mounted on Air Products liquid nitrogen cryostats (−196 °C) or condensed with Ar on closed cycle liquid He cryostats from Air Products or Leybold-Heraeus at 10–15 K. Operating pressures in the pyrolysis systems were 10^{-3}–10^{-5} Torr. IR spectra were recorded on Perkin-Elmer 281 or Mattson Sirius 100 FTIR instruments, NMR spectra on Bruker WH 400 or JEOL GX 400 instruments, and mass spectra on Varian MAT CH7a or 711 or Kratos MS25RFA instruments. In listings of ^{1}H NMR spectral data, each signal integrates as one proton, unless otherwise indicated. Chemicals Abstracts numbering is used. For mass spectra, electron ionization (EI) or field desorption (FD) were used as indicated. Melting points are uncorrected.

Benzothiet-2-one (5). Benzothiophene-2,3-dione (**9**) (150 mg) was sublimed from a flask held at 50 °C and pyrolyzed at 620 °C/10^{-3} Torr. A little polymer collected at the exit of the pyrolysis tube. Benzothietone (**5**) (94% yield based on subsequent NMR and reaction with methanol) was collected as a pale yellow solid on a cold finger (−196 °C). For IR spectroscopy (Figure 1) the sample was condensed on a KBr disk at −196 °C. For NMR spectroscopy $CDCl_3$ was condensed onto the sample at −196 °C, and on warming to −45 °C the solution was allowed to flow into a pre-cooled NMR tube: IR (film at −196 °C) 1856 (w), 1799 (s), 1712 (w), 1578 (m), 1564 (m), 1453 (w), 1431 (m), 1309 (w), 1268 (m), 1162 (w), 1141 (m), 1101 (w), 1042 (m), 997 (w), 815 (s), 760 (s), 724 (s), 701 (m), 667 (s), 627 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, −45 °C) δ 7.43 (t, ^3J = 7.7 Hz), 7.22 (d, ^3J = 7.6 Hz), 7.14 (t, ^3J = 7.7 Hz), 7.01 (d, ^3J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, −45 °C) δ 175.4 (dd, ^3J = 5 Hz, J = 2 Hz, C-2), 144.8 (t, ^3J = 7.7 Hz, C-2a), 143.7 (t, ^3J = 9.6 Hz, C-6a), 137.4 (dm, ^1J = 160 Hz, C-3), 126.1 (ddm, ^1J = 165 Hz, ^3J = 6.0 Hz, C-5), 121.6 (dm, ^1J = 167.3 Hz, C-6), 121.1 (dd, ^1J = 168.5 Hz, ^3J = 8.9 Hz, C-4).

Benzothiophene-2,3-dione (9). For comparison: IR (KBr) 1730 (m), 1715 (s), 1590 (s), 1525 (m), 1450 (s), 1310 (w), 1285 (s), 1220 (m), 1065 (w), 995 (m), 980 (w), 890 (s), 790 (w), 745 (s), 720 (w), 675 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.81 (ddd, ^3J = 7.6 Hz, ^4J = 0.5 Hz, ^4J = 1.2 Hz), 7.67 (td, ^3J = 7.6 Hz, ^4J = 1.5 Hz), 7.41 (dm, ^3J = 7.6 Hz), 7.36 (td, ^3J = 7.6 Hz, ^4J = 1 Hz); ^{13}C NMR ($CDCl_3$) δ 185.7 (s, C-2), 181.9 (d, ^3J = 3.3 Hz, C-3), 142.0 (t, ^3J

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(29) Kanakarajan, K.; Meier, H. *J. Org. Chem.* **1983**, *48* 881. Jacob, D.; Niedermann, H. P.; Meier, H. *Tetrahedron Lett.* **1986**, *27*, 5703–5706.
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= 9.2 Hz, C-7a), 138.3 (ddd, ^1J = 162.0 Hz, ^3J = 8.1 Hz, C-6), 128.3 (ddt, ^1J = 166.0 Hz, ^3J = 8.1 Hz, ^4J = 1.7 Hz, C-4), 127.6 (ddd, ^1J = 164.7 Hz, ^3J = 8.1 Hz, ^4J = 1.4 Hz, C-5), 125.8 (ddt, ^1J = 166.0 Hz, ^3J = 7.4 Hz, ^4J = 1.7 Hz, C-7).

Oligomerization of Benzothiet-2-one (5). Gentle warming of a 100-mg sample of **5** to −20 °C under vacuum caused the sample to sublime into a second cold trap. Warming to −20 °C under N_2 caused oligomerization to a solid, yellow film (mp 155–168 °C). On warming a 400-mg sample of **5** to −20 °C, the exothermicity of the oligomerization sufficed to partially melt and evaporate the sample. The resulting brown, glassy polymer had mp 138–159 °C. Oligomerization sets in at the thickest point of the sample.

The dimer (**6**) and trimer (**12**) were separated from polymer (**13**) by thick layer chromatography on SiO_2, eluting with $CHCl_3$. Yields: dimer, 13–29%; trimer, 6–15%; tetramer, not detectable; polymer, 81–56%. The dimer, trimer, and tetramer were prepared and separated according to ref 18 for comparison.

Dimer (6): mp 175–176 °C (lit.[18] mp 176–177 °C; lit.[19] mp 182–183 °C); IR (KBr) 3090 (w), 3060 (w), 1680 (s), 1580 (w), 1460 (w), 1426 (m), 1245 (m), 1202 (s), 1060 (w), 930 (s), 920 (s), 865 (w), 770 (m), 762 (s), 742 (m), 645 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 2 H), 7.25 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 196.8 (s), 142.2 (t, ^3J = 7.3 Hz), 135.4 (dd, ^1J = 165 Hz, ^3J = 7.3 Hz), 130.9 (dd, ^1J = 163.6 Hz, ^3J = 7.4 Hz), 130.7 (dd, ^1J = 163.6 Hz, ^3J = 8.1 Hz), 126.4 (dd, ^1J = 164.3 Hz, ^3J = 8.1 Hz), 125.0 (t, ^3J = 8.8 Hz); MS (EI), *m/z* (relative intensity) 272 (19.4), 228 (7.8), 180 (10.9), 152 (4.1), 136 (100), 108 (30.2), 82 (5.7), 69 (13.1).

Trimer (12): mp 255–257 °C (lit.[18] mp 257–258 °C); IR (KBr) 3090 (w), 3060 (w), 1695 (s), 1580 (w), 1460 (w), 1438 (m), 1280 (w), 1260 (w), 1205 (s), 1060 (m), 945 (w), 900 (s), 865 (m), 760 (m), 755 (s), 710 (m), 645 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.60 (m); ^{13}C NMR ($CDCl_3$) δ 191.2 (d, ^3J = 4.4 Hz), 144.5 (t, ^3J = 4.4 Hz), 137.2 (dm, ^1J = 170.2 Hz), 131.2 (dd, ^1J = 163.5 Hz, ^3J = 7.4 Hz), 130.3 (dd, ^1J = 164.3 Hz, ^3J = 7.4 Hz), 127.3 (dm, ^1J = 164.3 Hz), 124.5 (t, ^3J = 7.4 Hz); MS (EI), *m/z* (relative intensity) 272 (7.9), 240 (2.5), 228 (3.6), 224 (16.1), 212 (3.2), 196 (28.0), 180 (39.1), 136 (88.5), 108 (38.0), 69 (18.9), 44 (100); MS (FD), *m/z* (relative intensity) 411 (7.2), 410 (12.7), 409 (20.9), 408 (100), 273 (1.0).

Tetramer: mp 285–288 °C (lit.[18] mp 288–290 °C); IR (KBr) 3080 (w), 1685 (s), 1580 (w), 1560 (w), 1460 (m), 1435 (w), 1285 (m), 1260 (m), 1205 (s), 1115 (w), 1065 (w), 900 (s), 765 (s), 740 (m), 710 (m), 645 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.91 (d), 7.66 (d), 7.58 (t), 7.50 (t); ^{13}C NMR ($CDCl_3$) δ 189.4 (d, ^3J = 4 Hz), 141.4 (t, ^3J = 7.1 Hz), 137.2 (dd, ^1J = 167.4 Hz, ^3J = 8.1 Hz), 132.0 (dd, ^1J = 164.0 Hz, ^3J = 8.1 Hz), 129.5 (dd, ^1J = 164.0 Hz, ^3J = 8.1 Hz), 128.6 (ddd, ^1J = 161.1 Hz, ^3J = 8.0 Hz, ^4J = 1.3 Hz), 126.0 (t, ^3J = 8.4 Hz).

Polymer (13): mp 138–168 °C (see above; depends on method of preparation); IR (KBr) 3090 (w), 1680 (s), 1580 (w), 1560 (w), 1455 (m), 1425 (m), 1280 (m), 1200 (s), 1120 (w), 895 (s), 760 (s), 730 (s), 705 (s), 640 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) (broad peaks) δ 7.83 (d), 7.55 (d), 7.42 (m), 7.37 (m); ^{13}C NMR ($CDCl_3$) (broad peaks) δ 189.0, 141.0, 137.0, 131.8, 129.6, 128.9, 125.5. Anal. Calcd for C_7H_4OS: C, 61.74; H, 2.96. Found: C, 61.41; H, 2.96.

Reaction with Methanol. Methyl 2-Mercaptobenzoate (7) and Disulfide 11. Methylene chloride (2 mL) was distilled onto benzothietone (**5**) (207 mg, 1.52 mmol) that had been condensed on a cold finger coated with another 2 mL of CH_2Cl_2 at −196 °C. The cold finger was allowed to warm slowly, causing the solution to flow into 20 mL of CH_3OH cooled to −196 °C. The flask was then warmed to room temperature, the contents were stirred for 10 min, and the solvent was removed under vacuum. The product was dissolved in $CDCl_3$ and examined by NMR spectroscopy which revealed **7** (85%), **11** (9%), and traces of the dimer (**6**) and the trimer (**12**). Stirring of this solution for 12 h in the open air causes oxidation of 80% of **7** to the disulfide **11**.

7: IR (KBr) 2540 (m), 1700 (s), 1660 (m), 1430 (m), 1270 (m), 1210 (m), 1060 (w), 965 (w), 875 (m), 780 (w), 740 (m), 710 (w), 660 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.97 (d, ^3J = 7.6 Hz), 7.28 (m, 2 H), 7.11 (ddd, ^3J = 8.3 Hz, ^3J = 6.1 Hz, ^4J = 2.4 Hz), 4.80 (s), 3.90 (s); ^{13}C NMR ($CDCl_3$) δ 166.7, 137.9, 132.2, 131.4, 130.6, 125.2, 124.4, 52.5.

11: ^{1}H NMR ($CDCl_3$) δ 8.05 (dd, ^3J = 7.9 Hz, ^4J = 1.7 Hz), 7.75 (dm, ^3J = 8.0 Hz), 7.40 (tm), 7.23 (tm), 3.98 (s, 3 H); MS (EI), *m/z* 334 (M^+).

Naphtho[2,3-*b*]thiophene-2,3-dione (20). Because of some incompleteness in the description of the synthesis of this compound in the older literature,[32,33] a full procedure is given here. 3-Mercapto-2-naphthoic acid (**19**)[34] (4.1 g, 20 mmol) was dissolved in 100 mL of 2 N NaOH. Chloroacetic acid (3.7 g; 50 mmol) was added with stirring, followed by 2.6 g of solid NaOH. The mixture was maintained at 100 °C for 1 h, cooled to 0 °C, and adjusted to pH 3. The crude 3-carboxy-2-naphthalenemercaptoacetic acid precipitated as a white, amorphous mass, which was filtered and washed with a small amount of ice water; yield 4.5 g (87%), mp 174 °C (lit.[32] mp 175–176 °C). The product can be recrystallized from acetic acid, but this is not required for the following transformation.

The foregoing 3-carboxy-2-naphthalenemercaptoacetic acid (2.6 g, 10 mmol) was mixed with 8 g of solid NaOH and 3 mL of H_2O in a 500-mL flask fitted with a side arm for later introduction of N_2. The mixture was heated to 140 °C with stirring to produce a melt, and this was kept at 140 °C for 3 h, after which time it had turned orange. After cooling to 90 °C the air was replaced by N_2 and a steady stream of N_2 was maintained throughout the remaining operations. Oxygen-free boiling water (200 mL) was added slowly with constant stirring. A yellow solution was obtained. [The presence of air will cause green coloration due to formation of thioindigo]. After cooling to 40 °C and adjusting the pH to 12–13, the resulting solution of naphtho[2,3-*b*]thiophen-3-one (5,6-benzothioindoxyl) can be used in the subsequent transformation. The pure substance can be precipitated at pH 3–4 and recrystallized from ethanol (yellow plates, mp 141–142 °C (lit.[35] mp 140 °C)).

The foregoing naphtho[2,3-*b*]thiophen-3-one solution (pH 12–13; 40 °C; N_2 atmosphere) was treated with 4.5 g (30 mmol) of *p*-nitroso-*N*,*N*-dimethylaniline dissolved in a little ethanol. The mixture was constantly stirred and rapidly turned brown. After 1 h at 40 °C, cooling to 20 °C, filtering, and washing the solid several times on the filter with boiling water, 2-[*p*-(dimethylamino)phenyl]iminonaphtho[2,3-*b*]thiophen-3-one was obtained (0.52 g, 16%), mp 175 °C (lit.[33] mp 176 °C).

The foregoing anil (0.52 g) was dissolved in 20 mL of 60% (w/w) H_2SO_4 with stirring. After 15 min at 45 °C, 200 mL of water was added. Crude naphtho[2,3-*b*]thiophene-2,3-dione (**20**) precipitated and was filtered, dried, and sublimed at 100 °C in high vacuum, yielding 0.3 g (91%) of red plates, mp 173 °C (lit.[33] mp 168 °C): IR (KBr) 3050 (w), 1740 (w), 1705 (s), 1675 (w), 1612 (m), 1590 (m), 1575 (w), 1500 (w), 1450 (w), 1330 (m), 1265 (w), 1210 (w), 1165 (m), 1150 (w), 1050 (m), 985 (m), 900 (m), 885 (m), 835 (m), 770 (m), 750 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.38 (s), 7.95 (d, J = 8.2 Hz), 7.78 (d, J = 8.2 Hz), 7.72 (s), 7.68 (t, J = 7.5 Hz), 7.55 (t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 186.7 (s, C-2), 182.8 (d, ^3J = 3.6 Hz, C-3), 138.3 (m, C-8a), 132.8 (d, ^3J = 9.4 Hz, C-9a), 131.6 (m, C-4a), 131.5 (dd, ^1J = 162.3 Hz, ^3J = 8.4 Hz, C-7), 131.3 (ddd, ^1J = 162.0 Hz, C-5), 131.0 (dd, ^1J = 165.2 Hz, ^3J = 5.0 Hz, C-4), 127.6 (dd, ^1J = 162.9 Hz, ^3J = 8.3 Hz, C-6), 127.6 (ddd, ^1J = 161.1 Hz, C-8), 124.0 (dd, ^1J = 164.7 Hz, ^3J = 5.0 Hz, C-9), 122.6 (d, ^3J = 7.1 Hz, C-3a). Anal. Calcd for $C_{12}H_6O_2S$: C, 67.28; H, 2.83. Found: C, 67.10; H, 2.92.

Naphtho[2,3-*b*]thiet-2-one (21). (a) 3-Mercapto-2-naphthoic acid (**19**)[34] (300 mg) was sublimed from a flask at 80–130 °C and pyrolyzed at 800 °C/10^{-3} Torr in the course of 3 h. The product **21** was collected on a cold finger (−196 °C) as bright yellow crystals (55 mg; 20%), mp ca. 85 °C (oligomerization).

(b) Naphtho[2,3-*b*]thiophene-2,3-dione (**20**)[36] (300 mg) was sublimed at 80 °C and pyrolyzed at 650 °C/10^{-3} Torr in the course of 4 h. The product **21** was collected as above (248 mg; 95%): mp ca. 85 °C (oligomerization); IR (KBr) 3040 (w), 1800 (s), 1670 (m), 1650 (m), 1610 (m), 1585 (m), 1500 (m), 1440 (m), 1320 (m),

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1250 (m), 1200 (w), 1130 (m), 1080 (m), 980 (m), 880 (m), 865 (m), 840 (m), 770 (m), 735 (m), 680 (m) cm^{-1}; ^1H NMR ($CDCl_3$, −40 °C) δ 7.78 (dd, ^3J = 8.1 Hz, H-4), 7.67 (dd, ^3J = 8.1 Hz, H-7), 7.55 (ddd, $J_{4,6}$ = 1.3 Hz, $J_{6,7}$ = 8.1 Hz, H-6), 7.45 (s, H-3), 7.43 (s, H-8), 7.41 (ddd, $J_{5,6}$ = 7.2 Hz, $J_{4,5}$ = 8.1 Hz, $J_{5,7}$ = 1.2 Hz, H-5); ^{13}C NMR ($CDCl_3$, −40 °C)[37] δ 177.7 (d, ^3J = 5.5 Hz, C-2), 146.1 (d, ^3J = 7.5 Hz, C-2a), 138.3 (m, C-7a), 135.7 (d, ^3J = 11 Hz, C-8a), 131.4 (m, C-3a), 130.8 (ddd, ^1J = 161.0 Hz, ^3J = 5.0 Hz, ^3J = 7.5 Hz, ^3J = 7.5 Hz, C-4), 129.6 (dd, ^1J = 161.8 Hz, ^3J = 8.5 Hz, C-6), 127.1 (ddd, ^1J = 162.0 Hz, ^3J = 5.3 Hz, ^3J = 5.6 Hz, C-7), 125.9 (dd, ^1J = 162.3 Hz, ^3J = 8.0 Hz, C-5), 120.8 (dd, ^1J = 166.6 Hz, ^3J = 5.2 Hz, C-3), 118.9 (dd, ^1J = 167.4 Hz, ^3J = 5.3 Hz, C-8); MS (EI), *m/z* (relative intensity) 188 ($[M + 2]^+$, 4.5), 187 ($[M + 1]^+$, 12.3), 186 (M^+, 100), 160 (4), 159 (11), 158 ($[M - CO]^+$, 55); high resolution MS, *m/z* 186.0139 (calcd for $^{12}C_{11}H_6O^{32}S$, 186.0139). Anal. Calcd for $C_{11}H_6OS$: C, 70.94; H, 3.25. Found: C, 70.67; H, 3.29.

Dinaphtho[2,3-*c*:2′,3′-*g*]-1,5-dithiocine-7,15-dione (22). Solid **21** (100 mg) was kept at 30 °C in vacuum for 3 weeks. Unchanged **21** was then removed by sublimation. The remaining solid was extracted with 3 × 5 mL of $CHCl_3$ and the extract evaporated to yield 10 mg (10%) of **22**. The same product was formed in low yield within minutes of dissolving **21**, e.g., in $CHCl_3$, at room temperature. The remainder was polymer.

22: mp 306–312 °C; IR (KBr) 3050 (w), 1675 (s), 1580 (w), 1500 (m), 1420 (w), 1370 (w), 1325 (w), 1265 (w), 1180 (m), 1055 (s), 915 (s), 850 (m), 810 (s), 750 (m), 735 (m), 690 (m), 605 (w); ^1H NMR ($CDCl_3$) δ 8.15 (s, H-5), 8.06 (s, H-16), 7.95 (m, H-4), 7.84 (m, H-1), 7.54 (m, 2 H, H-2 and H-3); MS (FD), *m/z* (relative intensity) 374 (10.3), 373 (26.6), 372 (100), 344 (3.2), 186 (6.8); calcd for $^{12}C_{22}H_{12}O_2{}^{35}S_2$ 372.0279, found 372.0268; calcd for $^{12}C_{21}{}^{13}CH_{12}O_2{}^{35}S_2$ 373.0313, found 373.0296; calcd for $^{12}C_{22}H_{12}O_2{}^{32}S^{34}S$ 374.0237, found 374.0255.

Methyl 3-Mercapto-2-naphthoate (23). **21** (10 mg) was dissolved in a mixture of 5 mL of CH_2Cl_2 (acid, base, and water free) and 1 mL of dry CH_3OH. After stirring for 5 min at room temperature and removal of the solvents under N_2, **23** was obtained in quantitative yield: IR (KBr) 3200 (w), 2970 (w), 2760 (w), 1710 (s), 1260 (m), 1575 (m), 1440 (m), 1430 (m), 1270 (s), 1225 (m), 1200 (m), 1130 (m), 1100 (m), 1080 (m), 1000 (m), 940 (m), 890 (m), 865 (m), 770 (m), 735 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.58 (s), 7.82 (d, ^3J = 8.2 Hz), 7.75 (s), 7.66 (d, ^3J = 8.3 Hz), 7.54 (t), 7.43 (t), 4.73 (s), 3.98 (s, 3H); MS (EI), *m/z* (relative intensity) 219 (8.5), 218 (61.7), 187 (31), 186 (100), 158 (50), 155 (15), 115 (33).

Disulfide 24. A sample of **23** was dissolved in $CDCl_3$ and stirred in the open air for 12 h, giving disulfide **24** in 90% yield. For comparison, this substance was also prepared by adaptation of the method reported in ref 38: mp 80 °C (colorless needles); ^1H NMR ($CDCl_3$) δ 8.65 (s), 8.16 (s), 7.86 (d, *J* = 7.8 Hz), 7.62 (d, *J* = 7.8 Hz), 7.44 (m, 2 H), 4.07 (s, 3 H).

Indene-2-thiocarboxylic Acid *O*-Methyl Ester (26). Methyl indene-2-carboxylate (**28**) (2 g, 11.5 mmol) was dissolved in 10 mL of absolute xylene, treated wtih 5.58 g (13.8 mmol) of 2,4-bis(4-methoxyphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetan (Lawesson's reagent), and heated for 5 h at 140 °C. After cooling, the product was chromatographed on silica gel (Woelm, 100–200 μm), eluting with CCl_4. The yellow substance was collected, giving 2.08 g (95%): mp 68 °C; ^1H NMR ($CDCl_3$) δ 3.84 (d, ^3J = 1.6 Hz, 2 H, CH_2), 4.2 (s, 3 H, CH_3), 7.30–7.36 (m, 2 H, H-5 and H-6), 7.46–7.48 (m, H-7), 7.52–7.54 (m, H-4), 7.73–7.75 (m, H-3); ^{13}C NMR ($CDCl_3$) δ 207.7 (C=S), 146.4 (C-2), 145.1 (C-7a), 143.1 (C-3a), 137.7 (C-3), 127.9 (C-6), 127.0 (C-4), 124.2 (C-5), 124.0 (C-7), 58.2 (CH_3), 40.1 (C-1); MS (EI), *m/z* (relative intensity) 192 ($[M + 2]^+$, 4.6), 191 ($[M + 1]^+$, 11), 190 (M^+, 100).

Observation and Trapping of 2-Thiocarbonyl-2*H*-indene (25). 3-Mercapto-2-naphthoic acid (**19**) and naphtho[2,3-*b*]-thiophene-2,3-dione (**20**) were separately pyrolyzed at 900 °C/10^{-3} Torr and the products condensed on a KBr disk at −196 °C or 15 K for IR spectroscopy. Thietone **21** was no longer observable, and a new weak band at 1742 cm^{-1} was ascribed to **25**. CO was observed at 2137 cm^{-1} at 15 K. Co-condensation of the pyrolysis products with methanol at −196 °C again permitted observation of the 1742 cm^{-1} species, and warm-up to −120 °C caused disappearance of this signal and appearance of a new IR spectrum due to **26**. After warming to room temperature, **26** was identified by comparison of the ^1H NMR spectrum with that reported above. IR of **26**: 3060 (w), 3040 (w), 2980 (w), 2940 (w), 1540 (m), 1450 (m), 1435 (m), 1385 (m), 1340 (m), 1300 (m), 1250 (m), 1225 (s), 1190 (m), 1150 (m), 1055 (m), 1035 (m), 1015 (m), 880 (m), 760 (s), 710 (m) cm^{-1}.

Observation and Trapping of Naphtho[2,3-*b*]oxet-2-one (31) and 2-Carbonyl-2*H*-indene (30). 3-Acetoxy-2-naphthoic acid (**32**)[39] was pyrolyzed at 700 °C/10^{-3} Torr, being sublimed into the apparatus at 140 °C. The product condensed at −196 °C and showed IR bands at 1893 and 1874 cm^{-1} (**31**) and 2127 cm^{-1} (**30**). The former bands remained stable to −40 °C, and the latter to −120 °C on warm-up. Co-condensation of the product with methanol and subsequent warm-up to room temperature followed by gas chromatographic separation on a SE 52 column and comparison of retention times, IR, and ^1H NMR spectra with authentic samples yielded methyl 3-hydroxy-2-naphthoate (**29b**) (20%) and methyl indene-2-carboxylate (**28**) (4%). Similar results were obtained on pyrolysis of **29a** and **33**. An increase in the pyrolysis temperature (up to 900 °C) caused a gradual increase of the intensity ratio of the IR bands ascribed to **30** and **31** and a concomitant increase in the ratio of methanol trapping products **28**:**29b** as monitored by gas chromatography. Similar pyrolysis of **26** at 800 °C/10^{-3} Torr gave IR bands (−196 °C) at 1742 cm^{-1} (**25**) and 2127 cm^{-1} (**30**) with the same temperature dependence as described for these species above.

Observation and Trapping of Naphtho[2,3-*b*]azet-2-one (36). (a) 3-Amino-2-naphthoic acid (**34a**) (500 mg, 2.67 mmol) was pyrolyzed at 850 °C/10^{-3} Torr in the course of 40 min. The majority of the product was condensed on the metal part of the Air Products cold end at −196 °C. Small portions were condensed on the KBr window attached to the cold end at 8-min intervals. IR spectroscopy (−196 °C) showed an intense band at 1778 cm^{-1} (**36**), stable on warm-up to 0 °C, and a weaker band at 2215 cm^{-1} due to **37** (see below).

(b) Using the same procedure as above, the cold end was allowed to warm to ca. −100 °C and then rinsed with dry, −80 °C cold methanol under N_2. The cold methanol solution was allowed to warm to room temperature, the solvent was removed under vacuum at 10 °C, and the resulting mixture was examined by gas chromatography (SE 30). Comparison of retention times and ^1H NMR spectra with authentic specimens revealed methyl 3-amino-2-naphthoate (**34b**)[41] (20%), 2-naphthylamine (**40**) (8%), and 2-cyanoindene (**37**)[40] (68%).

(c) IR observations similar to those reported in (a) were made on pyrolysis of either methyl 3-amino-2-naphthoate (**34b**)[41] or benzisatoic acid anhydride (**35**)[41] at 800 °C/10^{-3} Torr.

Naphtho[2,1-*b*]thiet-1-one (42). **41** (300 mg) was sublimed at 75 °C and pyrolyzed at 620 °C/10^{-3} Torr in the course of 4 h. The product **42** was collected on a cold finger as bright orange crystals (94% yield): mp (polymerization) above 40 °C; IR (KBr) 3040 (w), 1793 (s), 1640, (w), 1620 (w), 1580 (w), 1550 (m), 1500 (m), 1140 (m), 805 (m), 765 (m), 740 (m), 660 (m) cm^{-1}; ^1H NMR ($CDCl_3$, −40 °C) δ 7.99 (d, ^3J = 8 Hz, H-4), 7.80 (d, ^3J = 8 Hz, H-5), 7.76 (d, ^3J = 8 Hz, H-8), 7.55 (ddd, $J_{7,5}$ = 1.3 Hz, $J_{7,8}$ = $J_{7,6}$ = 8 Hz, H-7), 7.42 (d, $J_{3,4}$ = 8 Hz, H-3), 7.39 (ddd, $J_{6,8}$ = 1.2 Hz, $J_{6,7}$ = $J_{6,5}$ = 8 Hz, H-6); ^{13}C NMR ($CDCl_3$, −55 °C) δ 171.6 (s, C-1), 147.3 (d, ^3J = 11 Hz, C-2a), 138.9 (dd, ^1J = 162.1 Hz, C-4), 134.8 (m, C-8b), 131.3 (m, C-8a), 130.4 (dd, ^1J = 161.4 Hz, C-7 or C-6), 129.3 (dm, ^1J = 156.3 Hz, C-5), 126.4 (m, C-4a), 125.4 (dd, ^1J = 160.6 Hz, C-6 or C-7), 122.0 (dd, ^1J = 165.8 Hz, C-8), 120.0 (d, ^1J = 168.7 Hz, C-3); MS, (EI), *m/z* (relative intensity) 187 ($[M + 1]^+$, 11), 186 (M^+, 100), 158 (70), 114 (23), 113 (9), 93 (8), 79 (21). Anal. Calcd for $C_{11}H_6OS$: C, 70.94; H, 3.25. Found: C, 70.79; H, 3.33.

(37) For analysis of ^{13}C NMR spectra of naphthalene derivatives, see e.g. Kalinowski, H.-O.; Berger, S.; Braun, S. ^{13}C-NMR-Spektroskopie; Thieme: Stuttgart, New York, 1984.

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Dinaphtho[2,1-*b*:2′,1′-*f*]-1,5-dithiocine-8,16-dione (44). This compound was obtained in 20% yield by using the procedure described for the isomer **22** above: mp 320–325 °C; IR (KBr) 3060 (w), 1675 (s), 1490 (m), 1320 (m), 1210 (m), 1170 (s), 1030 (s), 935 (s), 895 (m), 860 (s), 745 (s), 645 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.87 (d, ^3J = 8.3 Hz, H-1), 7.60 (d, ^3J = 8.1 Hz, H-4), 7.59 (ddd, $^3J_{2,1}$ = 6.9 Hz, $^3J_{2,3}$ = 8.3 Hz, $^4J_{2,4}$ = 1.4 Hz, H-2), 7.50 (ddd, $^3J_{3,2}$ = 6.9 Hz, $^3J_{3,4}$ = 8.1 Hz, $^4J_{3,1}$ = 1.2 Hz, H-3), 7.38 (d, ^3J = 8.4 Hz, H-5), 7.08 (d, ^3J = 8.4 Hz, H-6); ^{13}C NMR ($CDCl_3$) δ 197.7 (s, *OC*-16), 139.7 (m, C-16a), 133.7 (m, C-16b or C-4a), 130.2 (dd, ^1J = 162 Hz, ^3J = 4.9 Hz, C-5), 129.6 (d, ^1J = 166.3 Hz, C-6), 128.6 (m, C-4a or C-16b), 128.3 (dd, ^1J = 161.7 Hz, ^3J = 8.2 Hz, C-2 or C-3), 128.1 (ddd, ^1J = 161.7 Hz, C-4), 128.0 (dd, ^1J = 162.3 Hz, ^3J = 8.2 Hz, C-3 or C-2), 124.7 (dd, ^1J = 161.4 Hz, ^3J = 7.2 Hz, C-1), 123.5 (d, ^3J = 10.5 Hz, C-6a); MS (FD), *m/z* (relative intensity) 374 ([M + 2]$^+$, 45), 373 ([M + 1]$^+$, 26), 372 (M$^+$, 100), 186 (13). Anal. Calcd for $C_{11}H_6OS$: C, 70.94; H, 3.25. Found: C, 71.09; H, 3.32.

Methyl 2-Mercapto-1-naphthoate (43) and Its Disulfide. These compounds were obtained from **42** in the same manner as described for **23** and **24** above. **43**: IR (KBr) 3060 (w), 2955 (w), 2560 (w), 1725 (s), 1505 (m), 1432 (m), 1280 (m), 1240 (s), 1210 (m), 810 (s), cm^{-1}, identified by comparison with authentic material. **43** was oxidized to the disulfide by stirring a methanol–chloroform solution in air for 12 h. The disulfide was isolated in 85% yield by thick layer chromatography (SiO_4/toluene); ^1H NMR ($CDCl_3$) δ 7.87 (d), 7.84 (d), 7.80 (d), 7.79 (d), 7.53 (ddd), 7.48 (ddd), 4.01 (s, 3 H, CH_3); MS (EI), *m/z* (relative intensity) 434 (M$^+$, 16), 218 (18), 217 (100), 202 (16), 187 (5), 186 (5), 158 (10), 115 (5).

3-(1-Indenylidene)naphtho[1,2-*e*]-1,3-dithiin-1(1*H*)-one (46a or 46b). **41** (250 mg) was sublimed at 80 °C and pyrolyzed at 750 °C/10^{-3} Torr during 3 h. Some naphthothietone (**42**) collected in a cold trap at −196 °C. **46a** and **46b** collected in the air cooled part of the trap at room temperature. The product was taken up in $CHCl_3$ and unreacted naphthothietone (**42**) allowed to polymerize. Thick layer chromatography (SiO_2/$CHCl_3$) gave **46** as a yellow crystalline powder (70% yield): mp 173–176 °C; IR (KBr) 3050 (w), 1635 (s), 1545 (m), 1495 (m), 1440 (m), 1360 (m), 1180 (m), 1080 (m), 1055 (m), 855 (m), 810 (m), 775 (m), 740 (s), 710 (m) cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 8.64 (d, ^3J = 8.7 Hz, H-10), 8.25 (d, ^3J = 8.6 Hz, H-6), 8.04 (d, ^3J = 8.1 Hz, H-7), 7.92 (m, H-4′ or H-7′), 7.74 (ddd, $^3J_{9,10}$ = 8.7 Hz, $^3J_{9,8}$ = 7.0 Hz, $^4J_{9,7}$ = 1.5 Hz, H-9), 7.70 (d, ^3J = 8.6 Hz, H-5), 7.64 (ddd, $^3J_{8,7}$ = 8.1 Hz, $^3J_{8,9}$ = 7.0 Hz, $^4J_{8,10}$ = 1.1 Hz, H-8), 7.37 (m, H-7′ or H-4′), 7.28 (m, 2 H, H-5′ and H-6′), 7.03 (d, ^3J = 5.5 Hz, H-2′), 6.96 (dd, ^3J = 5.5 Hz, ^4J = 0.5 Hz, H-3′); ^{13}C NMR ($CDCl_3$) δ 186.1 (s, *OC*-1), 144.1 (m), 139.9 (d, ^3J = 10.2 Hz, C-4a), 139.8 (m, C-10b), 134.4 (dd, ^1J = 162.0 Hz, ^3J = 5.4 Hz, C-6), 133.8 (m), 133.2 (m, C-10a), 132.6 (d, ^1J = 169.5 Hz), 130.8 (m, C-6a), 129.7 (dd, ^1J = 161.3 Hz, ^3J = 8.4 Hz, C-9 or C-8), 128.5 (ddd, ^1J = 162.4 Hz, C-7), 128.0 (dd, ^1J = 160.1 Hz, ^3J = 7.1 Hz), 126.8 (dd, ^1J = 161.4 Hz, ^3J = 8.5 Hz, C-8 or C-9), 126.7 (m), 126.1 (dd, ^1H = 165.6 Hz, ^3J = 6.7 Hz), 125.9 (dd, ^1J = 160.7 Hz, ^3J = 6.7 Hz), 125.8 (dd, ^1J = 172.1 Hz, ^3J = 3.6 Hz), 125.2 (m), 125.0 (d, ^1J = 165.6 Hz, C-5), 125.0 (dm), 121.7 (dm, ^1J = 161.5 Hz); MS (EI), *m/z* (relative intensity) 346 (2.7), 345 (5.3), 344 (21.2), 187 (3.0), 186 (15), 160 (5), 159 (13), 158 (100), 114 (10); high resolution MS, calcd for $^{12}C_{21}H_{12}O^{32}S_2$ 344.0329, found 344.0336; calcd for $^{12}C_{20}{}^{13}CH_{12}O^{32}S_2$ 345.0363, found 345.0361; calcd for $^{12}C_{21}H_{12}O^{32}S^{34}S$ 346.0288, found 346.0311. Anal. Calcd for $C_{21}H_{12}OS_2$: C, 73.23; H, 3.62. Found: C, 72.93; H, 3.65.

3-Cyclohexyl-2-(cyclohexylimino)-3,4-dihydronaphtho[2,3-*e*]-1,3-thiazin-4(2*H*)-one (47). **21** (20 mg, 0.108 mmol) was added to 0.5 g of dicyclohexylcarbodiimide (DCC) at 60 °C and the mixture was stirred at this temperature for 6 h. Excess DCC was removed by bulb-to-bulb vacuum distillation and the residue recrystallized from ethanol, giving 26.7 mg (63%) colorless crystals: mp 164–165 °C; IR (KBr) 2920 (s), 2840 (m), 1650 (s), 1610 (s), 1580 (m), 1330 (s), 1290 (s), 1200 (s), 760 (m), 740 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.82 (s, H-10), 7.91 (d, ^3J = 8.3 Hz, H-9 or H-6), 7.70 (d, ^3J = 8.3 Hz, H-6 or H-9), 7.60 (s, H-5), 7.54 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, H-7 or H-8), 7.45 (ddd, ^3J = 8.3 Hz, ^3J = 7.0 Hz, ^4J = 1.2 Hz, H-8 or H-7), 5.02 (tt, $^3J_{ax,ax}$ = 12 Hz, $^3J_{ax,eq}$ = 3.5 Hz, N(3)-*CH* in cyclohexyl), 3.63 (m, =N—*CH* in cyclohexyl), 2.53 (m, 2 H), 1.2–1.9 (m, 18 H); ^{13}C NMR ($CDCl_3$) δ 24.2 (tm, 2 C), 25.8 (tm), 25.9 (tm), 26.7 (tm, 2C), 29.6 (tm, 2 C), 33.3 (tm, 2 C), 59.0 (dm, =N—*CH* in cyclohexyl), 59.1 (dm, N(3)-*CH* in cyclohexyl), 122.5 (dd, ^1J = 162.5 Hz, ^3J = 4.9 Hz, C-5 or C-10), 123.5 (d, ^3J = 7.5 Hz, C-4a), 126.2 (dd, ^1J = 161.2 Hz, ^3J = 8.2 Hz, C-7 or C-8), 126.4 (ddd, ^1J = 161.8 Hz, C-6 or C-9), 127.3 (d, ^3J = 8.5 Hz, C-10a), 129.0 (dd, ^1J = 161.4 Hz, ^3J = 8.6 Hz, C-8 or C-7), 129.6 (ddd, ^1J = 160.9 Hz, C-9 or C-6), 131.3 (m, C-5a or C-9a), 132.5 (dd, ^1J = 164.6 Hz, ^3J = 4.5 Hz, C-10 or C-5), 135.1 (m, C-9a or C-5a), 140.3 (m, C-2), 163.2 (s, C-4); MS (EI), *m/z* (relative intensity) 393 ([M + 1]$^+$, 2.7), 392 (M$^+$, 10.6), 321 (2.0), 313 (2.4), 312 (8.3), 311 (41.7), 310 (10.7), 296 (10.5), 229 (14.9), 228 (69.5), 187 (18.8), 186 (100). Anal. Calcd for $C_{24}H_{28}N_2OS$: C, 73.43; H, 7.19; N, 7.14. Found: C, 73.20; H, 7.18; N, 7.15.

3-Cyclohexyl-3,4-dihydronaphtho[2,3-*e*]-1,3-thiazine-2,4-(2*H*)-dione (48). This compound was obtained in 48% yield by stirring **47** dissolved in a 3:1 mixture of 10% HCl and ethanol at room temperature for 12 h. The solvent was removed under vacuum and the residue recrystallized from ethanol. The same compound was also obtained from 3-mercapto-2-naphthoic acid and dicyclohexylcarbodiimide with subsequent hydrolysis by adaptation of the method given in ref 30: mp 172–173 °C; IR (KBr) 1670 (s), 1630 (s), 1330 (s), 1290 (s), 1190 (s), cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.93 (s), 7.98 (d, ^3J = 8.2 Hz), 7.77 (d, ^3J = 8.2 Hz), 7.67 (s), 7.62 (t, ^3J = 8.2 Hz, ^3J = 7.0 Hz), 7.53 (ddd, ^3J = 8.2 Hz, ^3J = 7.0 Hz), 5.02 (tt), 2.44 (m, 2 H), 1.2–1.9 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 25.3 (tm), 26.5 (tm, 2 C), 29.1 (tm, 2 C), 57.0 (dm), 120.9 (d, ^3J = 7.3 Hz, C-4a), 122.22 (dd, ^1J = 162.2 Hz, ^3J = 4.8 Hz, C-5 or C-10), 126.6 (ddd, ^1J = 162.1 Hz, C-9 or C-6), 126.8 (dd, ^1J = 161.7 Hz, ^3J = 8.3 Hz, C-7 or C-8), 126.9 (d, ^3J = 8.1 Hz, C-10a), 129.8 (ddd, ^1J = 161.7 Hz, C-6 or C-9), 129.9 (dd, ^1J = 162.3 Hz, ^3J = 8.5 Hz, C-8 or C-7), 131.4 (m, C-5a, or C-9a), 133.8 (dd, ^1J = 165.1 Hz, ^3J = 4.7 Hz, C-5 or C-10), 135.3 (m, C-9a or C-5a), 164.1 (m, C-2), 164.7 (d, ^3J = 5.9 Hz, C-4); MS (EI), *m/z* (relative intensity) 313 ([M + 2]$^+$, 2), 312 ([M + 1]$^+$, 6.5), 311 (M$^+$, 33.5), 229 (10), 188 (18), 187 (47), 186 (100), 158 (43).

2-Cyclohexyl-3-(cyclohexylimino)-2,3-dihydronaphtho[1,2-*e*]-1,3-thiazin-1(1*H*)-one (49). The preparation was analogous to that of **47**: yield 67%; colorless crystals; mp 152 °C; IR (KBr) 2920 (s), 2840 (s), 1650 (s), 1600 (s), 1590 (m), 1500 (m), 1450 (m), 1420 (m), 1340 (s), 1275 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.17 (d, ^3J = 8.8 Hz, H-10), 7.83 (d, ^3J = 8.6 Hz, H-6), 7.77 (d, ^3J = 8.1 Hz, H-7), 7.60 (ddd, ^3J = 8.8 Hz, ^3J = 6.9 Hz, ^4J = 1.5 Hz, H-9), 7.48 (ddd, ^3J = 8.1 Hz, ^3J = 6.9 Hz, ^4J = 1.1 Hz, H-8), 7.21 (d, ^3J = 8.6 Hz, H-5), 5.02 (tt, $^3J_{ax,ax}$ = 11.9 Hz, $^3J_{ax,eq}$ = 3.6 Hz, N(2)-*CH* in cyclohexyl), 3.62 (m, =N—*CH* in cyclohexyl), 2.48 (m, 2 H), 1.2–1.9 (m, 18 H); ^{13}C NMR ($CDCl_3$) δ 24.2 (tm, 2 C), 25.8 (tm), 26.7 (tm, 2 C), 29.8 (tm, 2 C), 33.5 (tm, 2 C), 58.8 (dm, =N—*CH* in cyclohexyl), 59.6 (dm, N(2)-*CH* in cyclohexyl), 121.2 (m, C-10b), 122.6 (d, ^1J = 164.6 Hz, C-5) 126.0 (dd, ^1J = 160.9 Hz, ^3J = 8.5 Hz, C-8 or C-9), 126.5 (dd, ^1J = 166.2 Hz, ^3J = 6.6 Hz, C-10), 128.4 (dd, ^1J = 160.6 Hz, ^3J = 8.1 Hz, C-9 or C-8), 128.5 (ddd, ^1J = 159.5 Hz, C-7), 132.6 (m, C-6a and C-10a), 132.9 (d, ^3J = 10.2 Hz, C-4a), 132.9 (dd, ^1J = 161.5 Hz, ^3J = 5.4 Hz, C-6), 140.2 (dd, C-3), 164.2 (s, C-1); MS (FD), *m/z* (relative intensity) 394 ([M + 2]$^+$, 17.4), 393 ([M + 1]$^+$, 51.5), 392 (M$^+$, 100), 391 (12.3). Anal. Calcd for $C_{24}H_{28}N_2OS$: C, 73.43; H, 7.19; N, 7.14. Found: C, 73.24; H, 7.17; N, 7.19.

2-Cyclohexyl-2,3-dihydronaphtho[1,2-*e*]-1,3-thiazine-1,3-(1*H*)-dione (50). This compound was obtained in the same manner as described for **48** above: yield 42%; mp 174 °C; IR (KBr) 3040 (w), 2920 (m), 2850 (m), 1675 (s), 1640 (s), 1505 (m), 1420 (m), 1390 (m), 1330 (m), 1270 (m), 1250 (m), 1195 (m), 1120 (m), 805 (s), 790 (m), 750 (m) cm^{-1}; MS (EI), *m/z* (relative intensity) 311 (M$^+$, 6), 230 (6), 229 (2), 188 (5), 187 (15), 186 (100).

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86163-66-8; **32**, 5464-07-3; **33**, 1734-00-5; **34a**, 5959-52-4; **34b**, 21597-54-6; **35**, 29753-32-0; **36**, 86163-67-9; **37**, 29005-25-2; **40**, 91-59-8; **41**, 35051-46-8; **42**, 85601-43-0; **43**, 85601-44-1; **43** (disulfide), 109151-47-5; **44**, 109181-89-7; **46a**, 109151-49-7; **46b**, 109151-48-6; **47**, 109151-50-0; **48**, 109151-51-1; **49**, 109151-52-2; **50**, 109151-53-3; DCC, 538-75-0; *p*-nitroso-*N*,*N*-dimethylaniline, 138-89-6; chloroacetic acid, 79-11-8; 3-carboxy-2-naphthalenemercaptoacetic acid, 64289-70-9; naphtho[2,3-*b*]thiophen-3-one (5,6-benzothioindoxyl), 4735-10-8; 2-[*p*-(dimethylamino)-phenyl]iminonaphtho[2,3-*b*]thiophen-3-one, 109151-55-5.

Alkylation of Heteroaryl Halides by 2:1 Grignard Reagent/Cu(I) Mixtures. Synthesis of Alkylated Octahydrodibenzo[*b*,*j*][1,10]phenanthrolines

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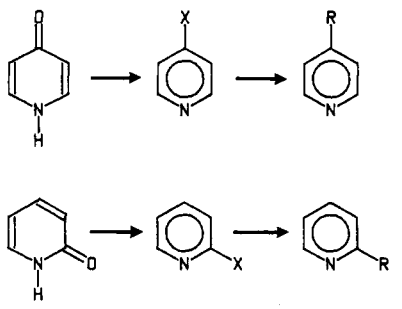
Treatment of 2-bromopyridine, 3-bromopyridine, 2-chloroquinoline, and 5,8-dichloro-1,2,3,4,9,10,11,12-octahydrodibenzo[*b*,*j*][1,10]phenanthroline (**2**) with a fourfold excess of 2:1 Grignard reagent/Cu(I) salt mixtures gives alkylated products in 50–85% yield. Thus prepared are 2-methylpyridine, 2-*tert*-butylpyridine, 3-*tert*-butylpyridine, 2-methylquinoline, 2-ethylquinoline, 2-*tert*-butylquinoline, and the dimethyl- and di-*tert*-butylphenanthrolines **3a** and **3b**. Full experimental details are provided for the two phenanthrolines, which are prepared in four steps from *o*-phenylenediamine and ethyl 1-oxocyclohexane-2-carboxylate in 25–30% overall yield.

The preparation of C-alkylated pyridine derivatives is a frequently encountered problem in synthesis of heterocyclic natural products, pharmaceuticals, and ligands. Whereas reduced 2-alkyl- and 4-alkylpyridines are available from pyridinium species,[1] the most general method for alkylation of heterocyclic halides is reaction with Wittig reagents.[2] Since annelated pyridones (e.g. quinolones) are obtained by various condensations[3] and are readily converted into halopyridines, the alkylation of heterocyclic halides completes an effective synthetic strategy (Scheme I). Numerous methods have been applied to the direct coupling of heteroaryl halides with alkylorganometallic reagents,[4] but these procedures are not entirely general. For example, nickel and palladium catalysts often lead to elimination of secondary and tertiary Grignard reagents, accompanied by reduction of the aryl halide.[4b,c] We report here a more widely applicable method for Grignard alkylation of 2-halo, 3-halo, and 4-halo heterocycles, providing examples from the pyridine, quinoline, and 1,10-phenanthroline series.

Results

Our requirement for 5,8-dialkyl-1,2,3,4,9,10,11,12-octahydrodibenzo[*b*,*j*][1,10]phenanthrolines as synthetic intermediates and potentially useful ligands led to the strategy outlined in Scheme II. Facile entry to the dibenzo[*b*,*j*][1,10]phenanthroline ring system is provided by Conrad–Limpach condensation of *o*-phenylenediamine with ethyl 1-oxocyclohexane-2-carboxylate, as described by Ege and Freund.[5] We have found that both steps are sensitive to reaction conditions, so complete details have been included in the Experimental Section. In particular, the neat condensation of *o*-phenylenediamine with ethyl 1-oxocyclohexane-2-carboxylate must be prolonged for weeks, if not months, to permit complete reaction. The crude intermediate is then heated at 220–230 °C in diphenyl ether, while the evolved ethanol is rapidly removed in a stream of nitrogen. This procedure affords the insoluble 1,10-phenanthroline-5,8-dione **1** in 48% overall yield. If the initial condensation step is conducted in refluxing benzene or methylene chloride then **1** does not crystallize from diphenyl ether after pyrolysis of the crude intermediate.

Scheme I



Direct treatment of diketone **1** with methyllithium, butyllithium, and Grignard reagents failed to produce significant quantities of the desired 5,8-dialkyl-1,10-phenanthrolines **3**. This necessitated a two-step alkylation procedure via a dihalide, as shown for the general case in Scheme I. We found that dichlorophenanthroline **2** could be prepared in high yield by heating **1** in phosphorus oxychloride (Scheme II). Hence, further efforts focused on

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