Filtration, removal of the solvent, and crystallization from alcohol yielded 12.7 g of product, mp 149–151° (lit.[21] 145°).

Anal. Calcd for $C_7H_3N_3O_4$: C, 43.54; H, 1.57; N, 21.76. Found: C, 43.46; H, 1.50; N, 21.74.

2,6-Dinitro-*p*-tolunitrile.—A solution containing 18 g of 4-chloro-3,5-dinitrotoluene (0.083 mol) and 15 g of cuprous cyanide (0.167 mol) in 150 ml of *N*,*N*-dimethylacetamide was stirred and heated at 130–135° for 1 hr. The mixture was cooled and poured into ice water. The crude product was collected by filtration, dried, and triturated with 500 ml of hot ethyl acetate. Filtration, removal of the solvent, and crystallization from alcohol yielded 10.9 g of product, mp 105–107° (lit.[22] 103°).

Anal. Calcd for $C_8H_5N_3O_4$: C, 46.39; H, 2.43; N, 20.29. Found: C, 46.32; H, 2.39; N, 20.01.

α,α,α-Trifluoro-2,6-dinitro-*p*-tolunitrile.—A solution containing 95 g of 4-chloro-3,5-dinitrobenzotrifluoride[23] (0.35 mol) and 35 g of cuprous cyanide (0.39 mol) in 200 ml of DMF was heated at 100° for 3.5 hr. The mixture was cooled and poured into ice water. The crude product was collected, dried, and triturated with hot ethyl acetate. Filtration, removal of the solvent, and crystallization from benzene yielded 60 g of product, mp 94–96°.

Anal. Calcd for $C_8H_2F_3N_3O_4$: C, 36.80; H, 0.77; N, 16.09. Found: C, 37.02; H, 0.91; N, 16.37.

(21) S. Reich, *Ber.*, **45**, 804 (1912).
(22) A. Claus and C. Beysen, *Ann.*, **266**, 223 (1891).
(23) L. M. Yagupol'skii and V. S. Mospan, *Ukr. Khim. Zh.*, **21**, 81 (1955); *Chem. Abstr.*, **49**, 8866 (1955).

Registry No.—2,6-Dinitrobenzonitrile, 35213-00-4; 2,6-dinitro-*p*-tolunitrile, 35213-01-5; α,α,α-trifluoro-2,6-dinitro-*p*-tolunitrile, 35213-02-6.

Acknowledgments.—The author wishes to thank Mr. Paul Unger and associates for spectral measurements and Mr. George Maciak and associates for microanalytical data.

The 1,2-Dithiolium Cation. XI.[1a] Polycyclic Dithiole and "No-Bond Resonance" Compounds[1b]

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The first known tricyclic 1,2-dithiolium salts **11**, **12**, and **13** have been prepared. The preparation of polycyclic thiothiophthene derivatives from these and related compounds is discussed.

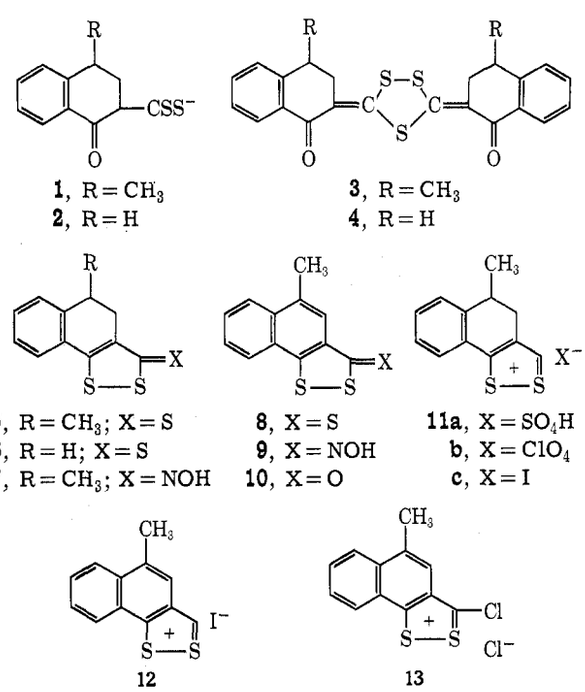
Recent investigations on the thiothiophthene "no-bond resonance" system have been facilitated by discoveries of attractive preparative methods based on condensation reactions of 1,2-dithiolium salts or other dithioles.[2] The present paper describes the preparation of certain bicyclic and tricyclic dithioles and the conversion of some of them to polycyclic thiothiophthene derivatives.

The investigation began with the application to 4-methyl-1-tetralone of the Thuillier–Vialle synthesis[3] of 1,2-dithiole-3-thiones. After base-catalyzed addition of carbon disulfide to give the dithiocarboxylic acid salt **1**, isolation from solution was effected by hypoiodite oxidation rather than the more usual procedures of acidification or alkylation. Analysis and molecular weight determination showed that the product thus obtained was the trithiolane **3**; it reacted smoothly with phosphorus pentasulfide to give the 1,2-dithiole-3-thione **5**, which was aromatized to **8** by sulfur at 190°.

Tetralone reacted similarly to give **2**, **4**, and **6**, but in somewhat lower yield; these were not investigated further.

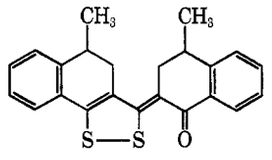
Although **5** and **8** are of course closely related, they belong to different families of dithiolethiones ("trithiones"), the aryl and benzo substituted, which differ in their behavior toward peracetic acid. The former are rapidly converted to high yields of aryl-1,2-dithiolium salts,[4] while the latter give poorly defined oxidation products which are not saltlike. Benzo-1,2-dithiolium salts are, in fact, obtainable only by an entirely different and circuitous method.[5] It is therefore of some interest that peracetic acid converts both **5** and **8** to the tricyclic dithiolium salts **11** and **12**, respectively. The latter was, to be sure, obtained in only modest yield and an impure state.

Hydroxylamine reacts with both **5** and **8**, giving oximes **7** and **9**, respectively, but mercuric acetate desulfuration succeeded only with **8**, giving **10**.

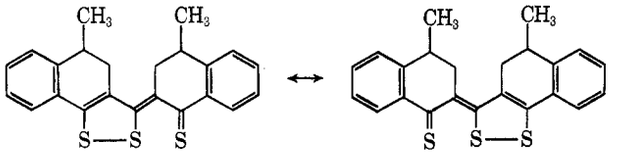


(1) (a) For paper IX, see E. Klingsberg, *Syn.*, 29 (1972). (b) Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.
(2) E. Klingsberg, *Quart. Rev.*, **23**, 537 (1969).
(3) A. Thuillier and J. Vialle, *Bull. Soc. Chim. Fr.*, 1398 (1959).
(4) E. Klingsberg, *J. Amer. Chem. Soc.*, **83**, 2934 (1961).
(5) A. Lüttringhaus, M. Mohr, and N. Engelhard, *Ann.*, **661**, 84 (1963).

Following a known method[6] for converting dithiolium salts to thiothiophthenes, **11a** was condensed with 4-methyltetralone to give **14**, which reacted with P_2S_5 to give the polycyclic thiothiophthene **15**. Attempts to dehydrogenate this to a completely aromatic system were unsuccessful.



14



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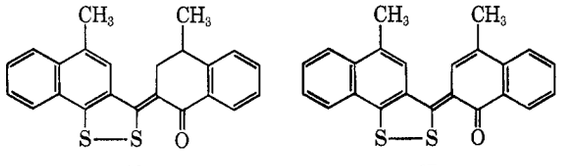
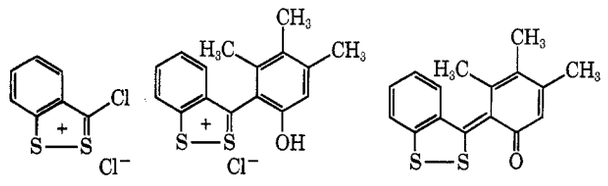


16 **17**

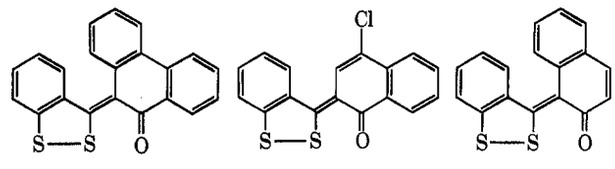
Like benzo-1,2-dithiole-3-thione, **8** reacted with sulfur dichloride to give a chlorodithiolium chloride **13**, which condensed with 4-methyl-1-tetralone to give **16** and with 4-methyl-1-naphthol to give **17**. The latter proved resistant to P_2S_5, again blocking the way to the fully aromatic system.

Similar results were given by a series of compounds prepared from 3-chloro-4,5-benzo-1,2-dithiolium chloride **18**.[7] Like 3-chloro-5-phenyl-1,2-dithiolium perchlorate,[8] **18** condensed readily with a series of phenolic compounds constituted for ortho substitution. The products, isolable as dithiolium salts such as **19**, were readily converted to pseudobases **20–23**. Reaction with P_2S_5 gave uniformly discouraging results. On the other hand, the partially saturated thiothiophthenes such as **28**, obtainable from **18** by condensation with cyclic ketones to dithioles **24–27** followed by P_2S_5 treatment, resisted attempts at aromatization. Similar difficulties have been encountered in the 3-phenyl-1,2-dithiole series.[9]

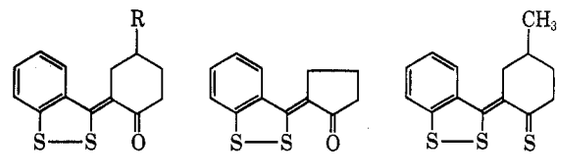
An unsuccessful attempt to devise a convenient synthesis for the little known 2-mercapto-1-naphthoic acid **29**, which would be a useful intermediate for the synthesis of naphthodithiole derivatives, began with the preparation of naphtho[2,1-*b*]thiophene-1,2-dione (**30**) from 2-naphthalenethiol and oxalyl chloride, a reaction that seems to have been reported only in the patent literature.[10] Good results are given by fusion at 170°; no catalyst is necessary. The product is readily isolated from the reaction mixture in 70% yield by virtue of its alkali solubility to give the sodium salt **31**, which regenerates **30** on acidification. The alkali-insoluble product consists of smaller yields of the hitherto unknown oxalic dithiol ester **32**.



18 **19** **20**



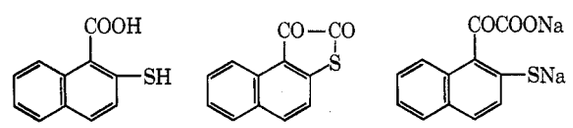
21 **22** **23**



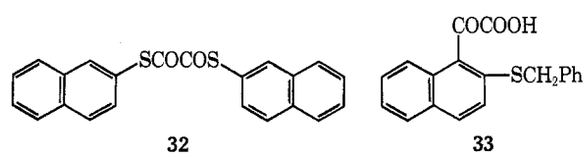
24, R = Me
25, R = Me_3C
26, R = H

27 **28**

No way could be found to eliminate a carbon atom from **30** or **31**, which are surprisingly stable. Prolonged boiling has no effect on **31**, and oxidation and decarboxylation experiments were unsuccessful. Benzylation of **31** gives **33**, which is converted to **30** by thionyl chloride.



29 **30** **31**



32 **33**

Experimental Section[11]

Trithiolane 3.—A 1.7 *M* solution of sodium *tert*-amylate was prepared by refluxing a mixture of 30.0 g of sodium ribbon and 88.0 g of *tert*-amyl alcohol in 500 ml of benzene for 24 hr. After filtration through glass wool to remove excess sodium, 259 ml (0.44 mol of sodium *tert*-amylate) of the solution was stirred in an ice bath while 32.0 g (0.20 mol) of 4-methyl-1-tetralone dissolved in 13.3 ml (0.22 mol) of carbon disulfide was added dropwise. A thick yellow slurry formed. After completion of addition, stirring was continued for 0.5 hr, followed by addition of 200 ml of water. The red aqueous layer was separated, and the benzene layer was washed twice with 200-ml portions of water. To the combined aqueous extracts was added, dropwise, 50.8 g (0.20 mol) of iodine dissolved in dilute sodium hydroxide. The copious yellow precipitate was filtered, washed free of base with water, and air dried, yield 28.3 g (65%), mp 195–200°. Crystallization from 360 ml of nitroethane yielded 17.7 g of bright orange crystals, mp 205–207°.

Anal. Calcd for $C_{24}H_{20}O_2S_3$: C, 66.0; H, 4.6; S, 22.0. Found: C, 65.8; H, 4.5; S, 22.0.

Results were similar when the reaction was performed on a much larger scale.

(6) E. Klingsberg, *J. Amer. Chem. Soc.*, **85**, 3244 (1963).
(7) J. Faust and R. Mayer, *Ann.*, **688**, 150 (1965).
(8) G. A. Reynolds, *J. Org. Chem.*, **33**, 3352 (1968).
(9) R. Pinel, Y. Mollier, and N. Lozac'h, *Bull. Soc. Chim. Fr.*, 856 (1967).
(10) German Patent 402,994 (1924); *Friedl.*, **14**, 474 (1924).
(11) Melting points are corrected.

Trithiolane **4** was prepared similarly. α-Tetralone (29.2 g, 0.20 mol) dissolved in 12.1 ml (0.20 mol) of carbon disulfide was dripped into 0.40 mol of sodium *tert*-amylate in benzene. After iodine treatment, a yield of 28.1 g (68%) of yellow solid, mp 225–226°, was obtained. Chlorobenzene gave orange crystals, mp 243–243.5°.

Anal. Calcd for $C_{22}H_{16}O_2S_8$: C, 64.6; H, 3.9; S, 23.5. Found: C, 64.4; H, 3.8; S, 23.3.

4,5-Dihydro-5-methyl-3*H*-naphtho[1,2-*c*]-1,2-dithiole-3-thione (5).—To a refluxing solution of 14.1 g (0.033 mol) of **3** in 200 ml of pyridine was added 22.5 g (0.101 mol) of P_2S_5. The mixture was refluxed 2.5 hr, cooled, diluted with ice water, chilled, and filtered, yield 11.8 g (71%) of deep orange solid, mp 105–107°. The compound crystallized from hexane with unchanged melting point.

Anal. Calcd for $C_{12}H_{10}S_3$: C, 57.6; H, 4.0; S, 38.4. Found: C, 57.6; H, 4.0; S, 38.5.

The dithiolethione **6** was prepared from **4** by refluxing with P_2S_5 for 1 hr in toluene, followed by filtration and evaporation. The gummy orange product was crystallized successively from methylcyclohexane and methanol, giving an orange product, mp 92–92.5°.

Anal. Calcd for $C_{11}H_8S_3$: C, 56.0; H, 3.4; S, 40.6. Found: C, 55.7; H, 3.7; S, 40.3.

5-Methyl-3*H*-naphtho[1,2-*c*]-1,2-dithiole-3-thione (8).—A mixture of 6.0 g (0.024 mol) of **5** and 1.58 g (0.048 g-atom) of sulfur was fused at 190° for 16 hr. The product was ground and crystallized from 50 ml of toluene to give 4.3 g (71%) of deep orange needles, mp 160–162°.

Anal. Calcd for $C_{12}H_8S_3$: C, 58.1; H, 3.2; S, 38.7. Found: C, 58.2; H, 3.1; S, 39.1.

5-Methyl-3*H*-naphtho[1,2-*c*]-1,2-dithiol-3-one Oxime (9).—A mixture of 0.50 g (2.0 mmol) of **8**, 0.20 g (2.9 mmol) of hydroxylamine hydrochloride, and 0.40 g (2.9 mmol) of sodium acetate trihydrate was stirred and refluxed in 50 ml of ethanol for 3 hr, slowly turning clear. Cooling and filtration gave 0.48 g (96%) of yellow product, mp 228–230°. Crystallization from dilute ethanol gave pale yellow product, melting point unchanged.

Anal. Calcd for $C_{12}H_9NOS_2$: C, 58.4; H, 3.6; N, 5.7; S, 25.9. Found: C, 58.6; H, 3.6; N, 5.5; S, 26.1.

Under similar conditions, **5** was converted in 65 hr of refluxing to a 76% yield of impure oxime **7**, mp 136–150°. Crystallization from methanol or hexane gave pale yellow product, mp 157–159°. Slow decomposition occurred on storage at room temperature.

Anal. Calcd for $C_{12}H_{11}NOS_2$: C, 57.9; H, 4.4; N, 5.6; S, 25.7. Found: C, 57.6; H, 4.4; N, 5.3; S, 26.0.

5-Methyl-3*H*-naphtho[1,2-*c*]-1,2-dithiol-3-one (10).—A suspension of 2.5 g (0.010 mol) of **8** in 200 ml of warm acetone was added to a solution of 4.0 g (0.013 mol) of mercuric acetate in 100 ml of acetic acid. The mixture was stirred at room temperature for 48 hr and then filtered to give a pale yellow solution. Dilution with water gave 1.75 g (76%) of pale yellow product, mp 126.5–127.5°. Crystallization from methylcyclohexane raised the melting point to 128–128.5°.

Anal. Calcd for $C_{12}H_8OS_2$: C, 62.1; H, 3.4; S, 27.6. Found: C, 61.9; H, 3.6; S, 27.5.

4,5-Dihydro-5-methylnaphtho[1,2-*c*]-1,2-dithiolium Hydrogen Sulfate (11a).—A solution of 24.0 g (0.096 mol) of **5** in 200 ml of acetone was immersed in an ice bath, and 54.0 g (0.288 mol) of 40% peracetic acid was added dropwise over a 2-hr period. Stirring was continued for 1 hr after addition was complete; this was followed by filtering and washing with cold acetone, to yield 25.8 g (85%) of bright yellow, water-soluble solid, mp 162–164°. It slowly decomposed on storage.

Anal. Calcd for $C_{12}H_{12}O_4S_3$: C, 45.6; H, 3.8; S, 30.4. Found: C, 45.8; H, 4.0; S, 30.6.

The corresponding perchlorate (**11b**) was prepared from **11a** in aqueous solution and crystallized from acetic acid or ethanol, mp 187.5–188.5°.

Anal. Calcd for $C_{12}H_{11}ClO_4S_2$: C, 45.3; H, 3.5; Cl, 11.1; S, 20.1. Found: C, 45.3; H, 3.4; Cl, 11.0; S, 20.2.

The orange iodide (**11c**) was crystallized from ethanol, mp 190–192° dec.

Anal. Calcd for $C_{12}H_{11}IS_2$: C, 41.6; H, 3.2; I, 36.7; S, 18.5. Found: C, 41.6; H, 3.2; I, 36.2; S, 18.2.

5-Methylnaphtho[1,2-*c*]-1,2-dithiolium Iodide (12).—A mixture of 1.24 g (5.0 mmol) of **8** and 1.7 g (15 mmol) of 30% hydrogen peroxide in 50 ml of acetic acid was stirred overnight at room temperature and then freed of solid by filtration. Addition of a little HI dissolved in acetic acid gave a brown precipitate, which was filtered, washed with ether, and further purified by trituration in benzene. The impure orange iodide weighed 0.65 g (38%) and melted at 104–107° dec.

Anal. Calcd for $C_{12}H_9IS_2$: I, 36.9; S, 18.6. Found: I, 34.5; S, 17.3.

Complete purification was not achieved and the product decomposed on storage.

Preparation of 14 from 11a.—A mixture of 15.9 g (0.050 mol) of **11a** and 6.4 g (0.040 mol) of 4-methyl-1-tetralone in 150 ml of ethanol was refluxed for 4 hr, cooled, and filtered, yield 6.9 g (46%) of red-brown solid. Crystallization from 300 ml of methylcyclohexane gave 3.8 g of bronze crystals, mp 176–178°. Additional crystallizations from methylcyclohexane and nitromethane gave bronze needles, mp 181–182°.

Anal. Calcd for $C_{23}H_{20}OS_2$: C, 73.5; H, 5.3; S, 17.0. Found: C, 73.4; H, 5.4; S, 17.0.

Conversion of 14 to 15.—To a refluxing solution of 3.8 g (0.010 mol) of **14** in 60 ml of chlorobenzene was added 3.3 g (0.015 mol) of P_2S_5. The mixture was stirred and refluxed for 0.5 hr, cooled to room temperature, and filtered. The filtrate was evaporated, yielding 4.1 g of slightly gummy purple product. Extraction in a Soxhlet apparatus with hexane gave 3.0 g of purple solid which was then stirred in dilute alkali for several hours, filtered, washed, and dried, yield 2.4 g (61.5%) of deep purple solid, mp 222–224°. Toluene gave deep purple crystals, mp 232–233.5°.

Anal. Calcd for $C_{23}H_{20}S_3$: C, 70.4; H, 5.1; S, 24.5. Found: C, 70.3; H, 5.3; S, 24.1.

Preparation of 3-Chloro-5-methylnaphtho[1,2-*c*]-1,2-dithiolium Chloride (13) and Conversion to 16.—Sulfur dichloride (3.0 ml) was added through the condenser to a stirred refluxing solution of 3.0 g (0.012 mol) of **8** in 90 ml of toluene. After 0.5 hr the product was cooled, filtered, and washed with benzene to yield 2.9 g (0.010 mol) of **13** as an orange solid. This was added to a solution of 1.7 g (0.011 mol) of 4-methyl-1-tetralone in 15 ml of toluene and stirred at reflux for 5.5 hr. Evaporation gave a red gum which was dissolved in toluene and chromatographed on a column of alumina. Elution with hexane followed by 75% benzene–25% methylcyclohexane gave 1.3 g (31%) of **16** as orange crystals, mp 170–171°. Crystallization from toluene or nitroethane raised the melting point to 173.5–175°.

Anal. Calcd for $C_{23}H_{18}OS_2$: C, 73.8; H, 4.8; S, 17.0. Found: C, 73.4; H, 5.1; S, 17.1.

Preparation of 17 from 13.—The chlorodithiolium chloride **13** (6.8 g, 0.027 mol) was added to a solution of 3.6 g (0.023 mol) of 4-methyl-1-naphthol in 90 ml of dry acetonitrile. After 24 hr of stirring at room temperature, the product was filtered and crystallized from 300 ml of butyl acetate to yield 2.8 g (33%) of purple needles, mp 215–216° dec.

Anal. Calcd for $C_{23}H_{16}OS_2$: C, 74.3; H, 4.3; S, 17.2. Found: C, 74.0; H, 4.2; S, 17.1.

3-Chlorobenzo-1,2-dithiolium Chloride (18).—To a stirred refluxing solution of 6.0 g (0.033 mol) of benzo-1,2-dithiole-3-thione[12] in 60 ml of benzene, 6.0 ml (9.7 g, 0.094 mol) of sulfur dichloride was carefully added, in portions, through the condenser. The mixture was stirred at reflux for 0.5 hr, cooled, and filtered. The yellow product was washed with carbon disulfide and transferred to a tared flask. After removal of traces of solvent by gentle warming, the yield was 6.5–7.0 g (87–94%). Results were similar on a large scale. It should be protected from moisture (which rapidly converts it to benzo-1,2-dithiol-3-one) and used as soon as possible.[7]

3-(2-Hydroxy-4,5,6-trimethylphenyl)benzo-1,2-dithiolium Chloride (19).—A mixture of 11.0 g (0.049 mol) of **18** and 6.8 g (0.050 mol) of 3,4,5-trimethylphenol in 125 ml of acetonitrile, sealed with a $CaCl_2$ tube to exclude moisture, was stirred at room temperature for 3.5 hr and then filtered. The yield of orange product, mp 244–245°, was 9.2 g (58%). It crystallized from acetic acid with unchanged melting point.

Anal. Calcd for $C_{16}H_{15}ClOS_2$: C, 59.6; H, 4.6; Cl, 11.0; S, 19.9. Found: C, 59.2; H, 4.6; Cl, 11.0; S, 19.4.

This was converted by dilute pyridine to the violet pseudobase **20** and crystallized from nitromethane followed by methylcyclohexane, mp 161–163°.

Anal. Calcd for $C_{16}H_{14}OS_2$: C, 67.2; H, 4.9; S, 22.4. Found: C, 67.2; H, 4.8; S, 22.1.

Pseudobase **21** was prepared by stirring 7.0 g (0.031 mol) of **18** and 5.0 g (0.026 mol) of 9-phenanthrol in 100 ml of acetonitrile

(12) E. Klingsberg and A. M. Schreiber, *J. Amer. Chem. Soc.*, **84**, 2941 (1962).

for 2 hr. The product was filtered, digested in dilute NaOH, filtered, washed, and dried, yielding 8.5 g (96%) of purple product, mp 202–203°. Crystallization from acetic acid, butyl acetate, or methylcyclohexane raised the melting point to 207–207.5°.

Anal. Calcd for $C_{21}H_{12}OS_2$: C, 73.3; H, 3.5; S, 18.6. Found: C, 73.4; H, 3.3; S, 18.4.

Pseudobase **22**, prepared similarly from 4-chloro-1-naphthol, crystallized from nitromethane as purple needles, mp 211.5–212°.

Anal. Calcd for $C_{17}H_9OS_2Cl$: C, 62.2; H, 2.7; Cl, 10.8; S, 19.5. Found: C, 62.1; H, 2.7; Cl, 10.7; S, 19.2.

Pseudobase **23**, prepared from 2-naphthol, contained a chlorinated by-product that was eliminated by chromatography of a methanol or nitromethane solution over alumina. The product was readily eluted, a reddish impurity being retained, and crystallized from methanol as purple needles, mp 162.5–163°.

Anal. Calcd for $C_{17}H_{10}OS_2$: C, 69.4; H, 3.4; S, 21.8. Found: C, 69.8; H, 3.2; S, 21.2.

2-(Benzo-1,2-dithiol-3-ylidene)-4-methylcyclohexanone (24).—A mixture of 22.0 g (0.099 mol) of **18** and 15.0 ml (13.7 g, 0.124 mol) of 4-methylcyclohexanone in 75 ml of toluene was stirred at reflux for 50 min, filtered hot, cooled, and chilled in Dry Ice–acetone, yielding 9.7 g (38%) of red-brown solid, mp 122–126°. Crystallization from 55 ml of acetic acid gave 7.5 g of red solid, mp 130–131.5°.

Anal. Calcd for $C_{14}H_{14}OS_2$: C, 64.1; H, 5.3; S, 24.4. Found: C, 64.1; H, 5.3; S, 24.6.

4-*tert*-Butylcyclohexanone gave yellow-red **25**, mp 164.5–165.5° (ethanol or methylcyclohexane).

Anal. Calcd for $C_{17}H_{20}OS_2$: C, 67.1; H, 6.6; S, 21.0. Found: C, 66.9; H, 6.5; S, 20.8.

Cyclohexanone gave orange-red **26**, mp 114.5–115° (hexane).

Anal. Calcd for $C_{13}H_{12}OS_2$: C, 62.7; H, 4.8; S, 25.8. Found: C, 62.7; H, 4.7; S, 25.7.

Cyclopentanone gave brown **27**, mp 149–151° (methylcyclohexane).

Anal. Calcd for $C_{12}H_{10}OS_2$: C, 61.5; H, 4.3; S, 27.3. Found: C, 61.2; H, 4.1; S, 27.2.

Thiothiophthene 28.—Phosphorus pentasulfide (4.50 g, 0.020 mol) was added to a refluxing solution of 4.18 g (0.016 mol) of **24** in 120 ml of toluene. The mixture was refluxed 1.5 hr, cooled, and filtered. The resulting olive-green solid was washed to a clear run-off with petroleum ether (bp 30–60°), dried, and stirred overnight in dilute alkali. Filtering, washing thoroughly with water, and drying gave 4.0 g of purple solid, mp 128–131°. Crystallization from methylcyclohexane or ethanol gave purple needles, mp 149.5–150°.

Anal. Calcd for $C_{14}H_{14}S_3$: C, 60.5; H, 5.0; S, 34.5. Found: C, 60.5; H, 5.1; S, 34.7.

Naphtho[2,1-*b*]thiophene-1,2-dione (30).—A mixture of 30.0 g (0.19 mol) of 2-naphthalenethiol and 45 ml (67 g, 0.53 mol) of oxalyl chloride was heated under reflux for 3 hr in an oil bath at 110–120°. The condenser was then set for distillation and heating continued for 1 hr at 165–175°. The product was cooled, ground, and subjected to prolonged or repeated digestion at room temperature with 1 *N* NaOH, which left undissolved 8.4 g (24%) of crude 2-naphthyl dithioloxalate (**32**), mp 170–200°. Crystallization from 280 ml of trichloroethylene gave 5.2 g (15%), mp 225–227°. It could also be crystallized from toluene or butyl acetate.

Anal. Calcd for $C_{22}H_{14}O_2S_2$: C, 70.6; H, 3.7; S, 17.1. Found: C, 70.2; H, 3.8; S, 17.2.

Acidification of the orange NaOH solution gave 28.0 g (70%) of red-orange **30**, mp 156–158°. A specimen crystallized from butyl acetate or methylcyclohexane melted at 158–159° (lit.[10] mp 153°).

Anal. Calcd for $C_{12}H_6O_2S$: C, 67.3; H, 2.8; S, 14.9. Found: C, 67.1; H, 2.9; S, 14.7.

2-Benzylthio-1-naphthaleneglyoxylic Acid 33.—To a boiling solution of 2.14 g (0.0100 mol) of **30** in 20 ml of 5 *N* NaOH, 20 ml of water, and 20 ml of ethanol, was added 1.50 ml (1.65 g, 0.0130 mol) of benzyl chloride. The solution turned from orange to pale yellow in 1–2 min and was then cooled and acidified. An oil formed and slowly changed to 3.2 g (100%) of yellow crystals, mp 110–113°. Crystallization from toluene or methylcyclohexane raised the melting point to 115–118°.

Anal. Calcd for $C_{19}H_{14}O_3S$: C, 70.8; H, 4.3; S, 9.9. Found: C, 70.5; H, 4.2; S, 9.7.

Refluxing for 1 hr with thionyl chloride in benzene, both of which were then evaporated, gave **30**.

Registry No.—**3**, 35051-21-9; **4**, 35051-22-0; **5**, 35051-23-1; **6**, 35051-24-2; **7**, 35051-25-3; **8**, 35051-26-4; **9**, 35051-27-5; **10**, 35051-28-6; **11a**, 35051-29-7; **11b**, 35051-30-0; **11c**, 35051-31-1; **12**, 35051-32-2; **14**, 35051-33-3; **15**, 35096-47-0; **16**, 32003-89-7; **17**, 34180-78-4; **19**, 35051-36-6; **20**, 32741-87-0; **21**, 34294-68-3; **22**, 34192-52-4; **23**, 34192-54-6; **24**, 32003-88-6; **25**, 32041-16-0; **26**, 32003-84-2; **27**, 32003-83-1; **28**, 35051-45-7; **30**, 35051-46-8; **32**, 35051-47-9; **33**, 35051-48-0.

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Kinetics of the Chromic Acid Oxidation of Deoxybenzoin[1]

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The kinetics of the chromic acid oxidation of deoxybenzoin has been examined in 91% acetic acid. The rate law is given by $v = k_1k_2[\text{ketone}][Cr^{VI}][H^+]^2/(k_{-1}[H^+] + k_2[Cr^{VI}])$ where k_1 was found to be equal to the rate of enolization. Benzoin was shown to be the intermediate in the reaction, and the source of the products, benzil, benzaldehyde, and benzoic acid. Substituent effects on the oxidation reaction and on enolization were found to be the same. When the concentration of chromium(VI) was maintained at a low level during the course of the reaction, bidesyl became a significant product. This suggests the formation of the desyl radical *via* a reaction involving an intermediate oxidation state of chromium.

The oxidation of ketones frequently provides a useful synthetic route to α-hydroxy ketones, α diketones, and carboxylic acids. As part of a continuing investigation of the mechanisms of chromic acid oxidations, we have studied the oxidation of deoxybenzoin. This is a convenient substrate in that the reaction site is localized by the flanking phenyl rings thus minimizing secondary reactions. Further, the compound provides an opportunity to examine substituent effects.

The chromic acid oxidation of ketones has received previous study. Umeda and Tarama[3] as well as Best, Littler, and Waters[4] have investigated the kinetics of the oxidation of cyclohexanone and found the rate to

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(2) Taken in part from the Ph.D. Thesis of O. Aniline, 1968.

(3) K. Umeda and K. Tarama, *Nippon Kagaka Zasshi*, **83**, 1216 (1962).

(4) P. A. Best, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, 822 (1962).