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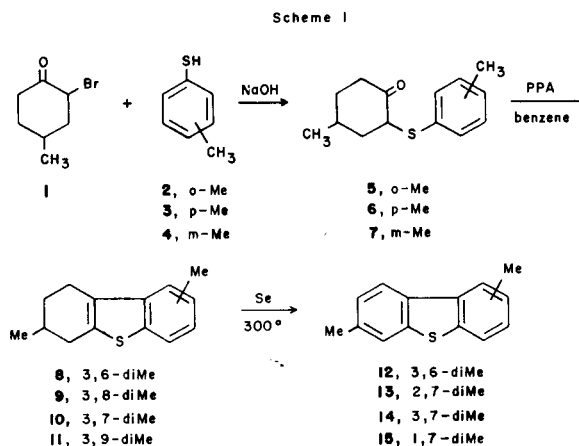
The synthesis of all four isomers of the monoethyldibenzothiophenes and all of the sixteen isomers of the dimethyldibenzothiophenes has been accomplished.

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In a paper by Wiley, Iwao, Castle and Lee [3] four different compounds of molecular weight 212 were shown to be present in shale oils, coal liquids and coal derived products. These correspond to either the monoethyldibenzothiophenes or the dimethyldibenzothiophenes. Therefore the synthesis of all four of the monoethyldibenzothiophenes and all sixteen of the dimethyldibenzothiophenes has been undertaken in order to determine unequivocally which of these isomers were present in the coal derived products referred to in reference [3]. This phase of the program to prepare all of the polycyclic thiophenes occurring in coal derived products follows those previously reported [4-18].

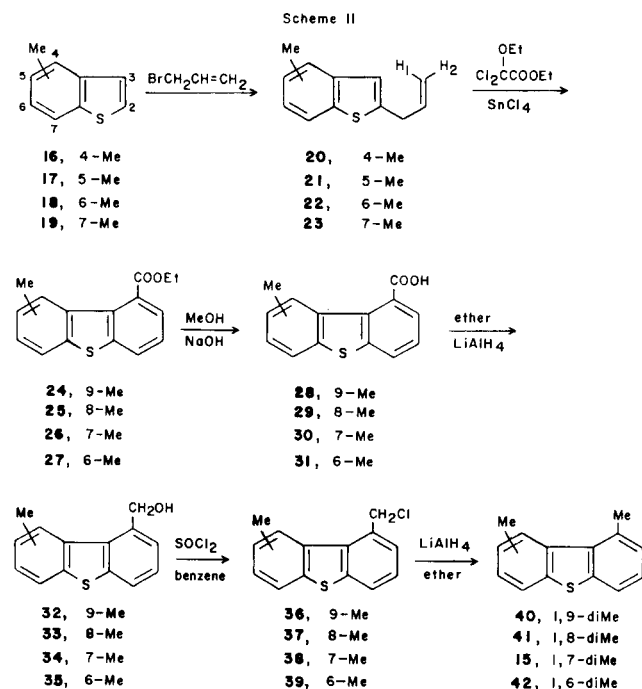
The reaction of 2-bromo-4-methylcyclohexanone (**1**) with *o*-methylbenzenethiol (**2**), with *p*-methylbenzenethiol (**3**) or with *m*-methylbenzenethiol (**4**) in the presence of sodium hydroxide *via* the methods of Campaigne *et al.* [19] and Fujiwara *et al.* [20] gave 2-(*o*-tolylthio)-4-methylcyclohexanone (**5**) in 83% yield, 2-(*p*-tolylthio)-4-methylcyclohexanone (**6**) in 87% yield, and 2-(*m*-tolylthio)-4-methylcyclohexanone (**7**) in 85% yield respectively. The polyphosphoric acid (PPA) cyclization of **5** gave 3,6-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**8**) in 69% yield. When **6** was cyclized with polyphosphoric acid (PPA), 3,8-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**9**) was obtained in 67% yield. When **7** was allowed to cyclize (PPA), an inseparable mixture of two products was obtained, namely, 3,7-dimethyl- (**10**) and 3,9-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**11**) in 69% combined yield. Aromatization of **8** was accomplished by heating at 300° with selenium. The product, 3,6-dimethyldibenzothiophene (**12**), was obtained in 75% yield. Conversion of **9** into 2,7-dimethyldibenzothiophene was accomplished in the same manner in 81% yield. When the mixture of **10** and **11** was allowed to aromatize with selenium at 300°, a mixture of 3,7-dimethyldibenzothiophene (**14**) and 1,7-dimethyldibenzothiophene (**15**) was obtained. Compound **14** had been previously prepared by Armarego and Davies [21]. Separation of **14** and **15** was accomplished by column chromatography on

neutral alumina using hexane as the eluent giving pure **14**. Further column chromatography on basic alumina using pentane as the eluent gave first additional pure **14** followed by pure **15**. The combined yield of **14** from the mixture of **10** and **11** was 41%. The yield of **15** from the mixture of **10** and **11** was 31%. Compound **14** was identical in all respects to that reported [21]. Compound **15** has also been prepared by an independent method described later in this paper. These transformations are outlined in Scheme I.

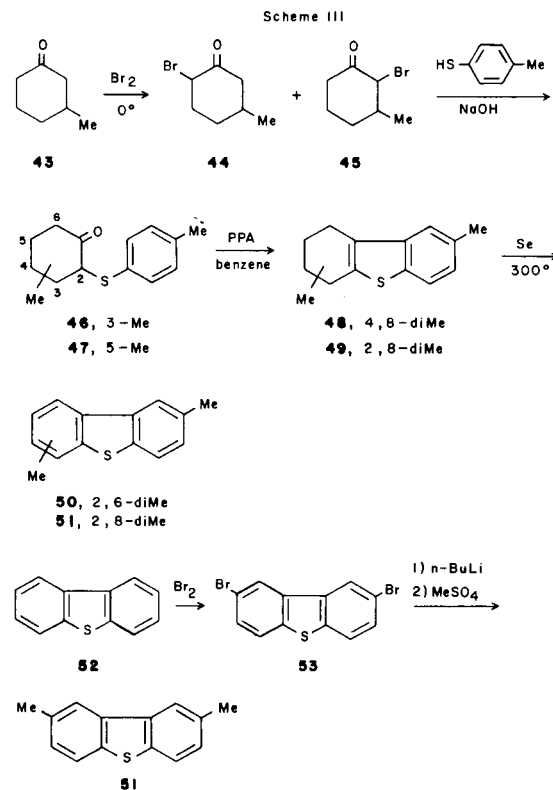


When 4-methylbenzo[*b*]thiophene (**16**) [22], 5-methylbenzo[*b*]thiophene (**17**) [22], 6-methylbenzo[*b*]thiophene (**18**) [23] or 7-methylbenzo[*b*]thiophene (**19**) [22] were allowed to react with *n*-butyllithium by the method of Meth-Cohn *et al.* [24] the corresponding 2-lithio derivatives were obtained. Treatment of the requisite lithio derivative with allyl bromide gave the following: 2-allyl-4-methylbenzo[*b*]thiophene (**20**) in 88% yield; 2-allyl-5-methylbenzo[*b*]thiophene (**21**) in 81% yield; 2-allyl-6-methylbenzo[*b*]thiophene (**22**) in 82% yield; and 2-allyl-7-methylbenzo[*b*]thiophene (**23**) in 75% yield respectively. Continuing with the method of Meth-Cohn *et al.* [24], compound **20**, **21**, **22** or **23** when allowed to react with stannic chloride and ethyl dichloroethoxyacetate [25] gave: ethyl 9-methyldibenzo-

thiophene-1-carboxylate (**24**) in 76% yield; ethyl 8-methyldibenzothiophene-1-carboxylate (**25**) in 79% yield; ethyl 7-methyldibenzothiophene-1-carboxylate (**26**) in 75% yield; and ethyl 6-methyldibenzothiophene-1-carboxylate (**27**) in 73% yield respectively. Methanolic sodium hydroxide hydrolysis of the esters **24**, **26**, **26** or **27** gave: 9-methyldibenzothiophene-1-carboxylic acid (**28**) in 90% yield; 8-methyldibenzothiophene-1-carboxylic acid (**29**) in 87% yield; 7-methyldibenzothiophene-1-carboxylic acid (**30**) in 92% yield; and 6-methyldibenzothiophene-1-carboxylic acid (**31**) in 88% yield respectively. Lithium aluminum hydride (LAH) reduction (dry ether) of the carboxylic acids **28**, **29**, **30** or **31** gave 1-hydroxymethyl-9-methyldibenzothiophene (**32**) in 95% yield; 1-hydroxymethyl-8-methyldibenzothiophene (**33**) in 93% yield; 1-hydroxymethyl-7-methyldibenzothiophene (**34**) in 95% yield; and 1-hydroxymethyl-6-methyldibenzothiophene (**35**) in 91% yield, respectively. Compound **32**, **33**, **34** or **35** reacted smoothly with thionyl chloride to give: 1-chloromethyl-9-methyldibenzothiophene (**36**) in 85% yield; 1-chloromethyl-8-methyldibenzothiophene (**37**) in 88% yield; 1-chloromethyl-7-methyldibenzothiophene (**38**) in 87% yield; and 1-chloromethyl-6-methyldibenzothiophene (**39**) in 90% yield, respectively. The reaction of **36**, **37**, **38** or **39** with LAH (dry ether) gave: 1,9-dimethyldibenzothiophene (**40**) in 88% yield; 1,8-dimethyldibenzothiophene (**41**) in 90% yield; 1,7-dimethyldibenzothiophene (**15**) in 89% yield; and 1,6-dimethyldibenzothiophene (**42**) in 88% yield respectively. This independent synthesis of **15** where the position of the methyl groups are unequivocal adds further evidence for the assignment of the structure of **15** (see above). These reactions are illustrated in Scheme II.

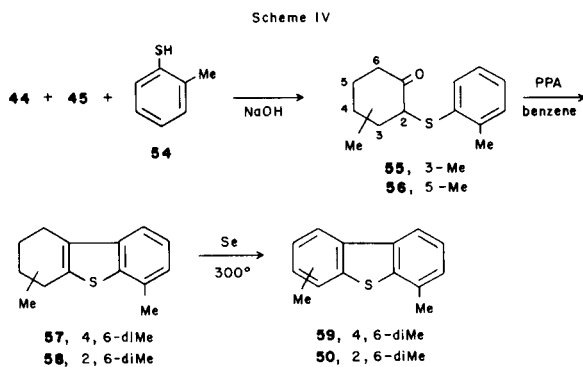


Bromination of 3-methylcyclohexanone (**43**) at 0° gave a mixture of 2-bromo-5-methylcyclohexanone (**44**) and 2-bromo-3-methylcyclohexanone (**45**) in near quantitative yield. When this mixture was allowed to react with *p*-methylbenzenethiol in sodium hydroxide solution (ethanol-water, 50-50) it gave a mixture of 2-(*p*-tolylthio)-3-methylcyclohexanone (**46**) and 2-(*p*-tolylthio)-5-methylcyclohexanone (**47**) in a yield of 80%. Cyclization (PPA in benzene) of the mixture of **46** and **47** gave a mixture of 4,8-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**48**) and 2,8-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**49**) in a 66% yield. Selenium aromatization at 300° of the mixture of **48** and **49** gave a mixture of 2,6-dimethyldibenzothiophene (**50**) and 2,8-dimethyldibenzothiophene (**51**). Separation of the mixture of **50** and **51** was achieved by column chromatography on neutral alumina using hexane as the eluent. Compound **51** eluted first in pure form. By this procedure the second fraction consisted of a mixture of **50** and **51** which was separated by column chromatography on basic alumina using pentane as the eluent. Compound **51** again eluted first in pure form and the combined yields of **51** from the two column chromatographs was 34%. This compound was reported previously by Campaigne and Ashby [26]. Compound **50** eluted last in pure form from the basic alumina column in a yield of 31%. 2,8-Dimethyldibenzothiophene (**51**) was also prepared by another method. Dibenzothiophene (**52**) was brominated by the method of Campaigne and Ashby [26] giving 2,8-dibromodibenzothiophene (**53**). Lithiation of **53** with *n*-butyllithium gave the dilithio deri-



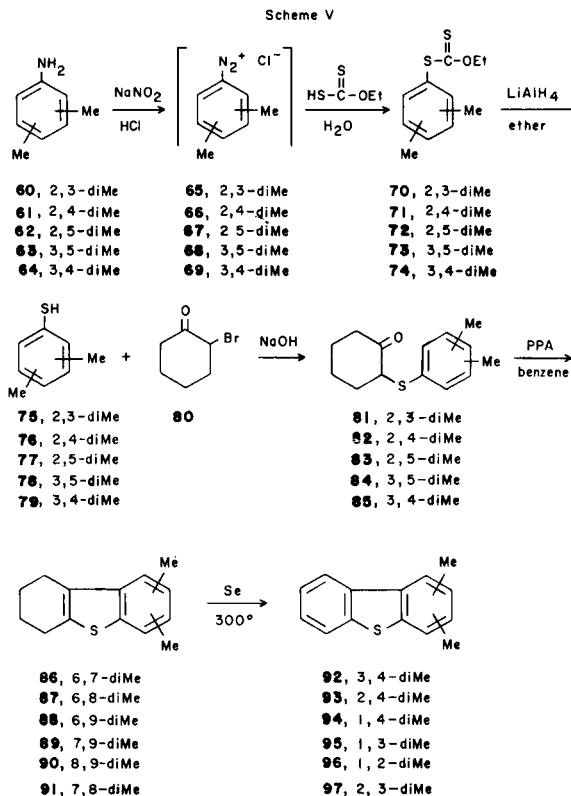
vative which upon treatment with dimethylsulfate produced 2,8-dimethyldibenzothiophene (**51**) in 28% yield (Scheme III).

When the mixture of **44** and **45** was allowed to react with *o*-methylbenzenethiol in the presence of sodium hydroxide in aqueous ethanol (50:50), the product was a mixture of 2-(*o*-tolylthio)-3-methylcyclohexanone (**55**) and 2-(*o*-tolylthio)-5-methylcyclohexanone (**56**) in combined yield of 78%. The mixture of **55** and **56** was cyclized with PPA in benzene solution producing a mixture of 4,6-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**57**) and 2,6-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**58**) in 69% combined yield. Selenium aromatization of the mixture of **57** and **58** gave a mixture of 4,6-dimethyldibenzothiophene (**59**) and 2,6-dimethyldibenzothiophene (**50**). Compound **59** has been previously reported by Gerdil and Lucken [27] and by Kruber and Raeithel [28]. Compound **50** was also prepared from other intermediates in this investigation (see above). Separation of **59** from **50** was accomplished by column chromatography on neutral alumina using hexane as the eluent. Compound **59** elutes first in pure form and was identical to **59** as previously reported [27,28]. The material remaining on the neutral alumina column was a mixture of **50** and **59**. Column chromatography on basic alumina gave additional pure **59** upon elution with pentane. The second fraction was pure **50** identical to that described above. These reactions are outlined in Scheme IV.



Diazotization of the following: 2,3-dimethylaniline (**60**), 2,4-dimethylaniline (**61**), 2,5-dimethylaniline (**62**), 3,5-dimethylaniline (**63**), and 3,4-dimethylaniline (**64**) gave **65**, **66**, **67**, **68**, **69** as intermediates which when treated with ethyl xanthate produced the following: 2,3-dimethylphenyl ethyl xanthate (**70**) in 98% yield; 2,4-dimethylphenyl ethyl xanthate (**71**) in 97% yield; 2,5-dimethylphenyl ethyl xanthate (**72**) in 98% yield; 3,5-dimethylphenyl ethyl xanthate (**73**) in 92% yield; and 3,4-dimethylphenyl ethyl xanthate (**74**) in 97% yield respectively. The reaction of **70**, **71**, **72**, **73** or **74** with LAH gave the following compounds: 2,3-dimethylbenzenethiol (**75**) [29] in 94% yield; 2,4-dimethylbenzenethiol (**76**) [29] in 93% yield; 2,5-dimethylbenzenethiol (**77**) [29] in 90% yield; 3,5-dimethyl-

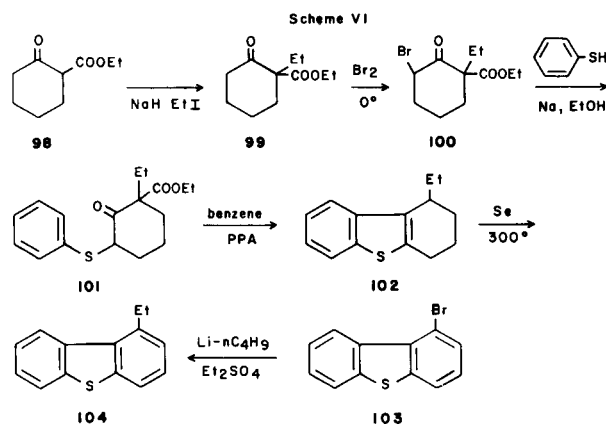
benzenethiol (**78**) [29] in 92% yield; and 3,4-dimethylbenzenethiol (**79**) [29] in 95% yield, respectively. Compounds **75**, **76**, **77**, **78** and **79** were prepared by the method reported by Osborne [30] for the synthesis of isomeric methylbenzenethiols. The yields which we report are nearly double those reported by Bartkus [29] using a different synthetic approach. Reaction of 2-bromocyclohexanone (**80**) with **75**, **76**, **77**, **78** or **79** in aqueous ethanolic sodium hydroxide solution gave the following: 2-(2,3-dimethylphenylthio)cyclohexanone (**81**) in 85% yield; 2-(2,4-dimethylphenylthio)cyclohexanone (**82**) in 84% yield; 2-(2,5-dimethylphenylthio)cyclohexanone (**83**) [20]; 2-(3,5-dimethylphenylthio)cyclohexanone (**84**) in 82% yield; and 2-(3,4-dimethylphenylthio)cyclohexanone (**85**) in 81% yield respectively. Cyclization (PPA) of **81**, **82**, **83** or **84** gave: 6,7-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**86**) in 84% yield; 6,8-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**87**) in 80% yield; 6,9-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**88**) [20]; 7,9-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**89**) in 78% yield respectively. Cyclization (PPA) of **85** gave a mixture of 8,9-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**90**) and 7,8-dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**91**) in a combined yield of 89%. Selenium aromatization of **86**, **87**, **88** or **89** gave: 3,4-dimethyldibenzothiophene (**92**) in 63% yield; 2,4-dimethyldibenzothiophene (**93**) [32] in 75% yield; 1,4-dimethyldibenzothiophene (**94**) [20] in 75% yield; and 1,3-dimethyldibenzothiophene (**95**) [32] in 71% yield respectively. The mixture of **90** and **91** upon selenium de-



hydrogenation gave a mixture of 1,2-dimethyldibenzothiophene (**96**) and 2,3-dimethyldibenzothiophene (**97**). Separation *via* column chromatography on neutral alumina gave pure **97** as the first fraction upon elution with hexane. The second fraction was a mixture of **96** and **97** which was separated by column chromatography on basic alumina using pentane as the eluent. Additional pure **97** was obtained in the first fraction. The total yield of the combined **97** was 32%. Further elution gave pure **96** in 28% yield. These transformations are outlined in Scheme V.

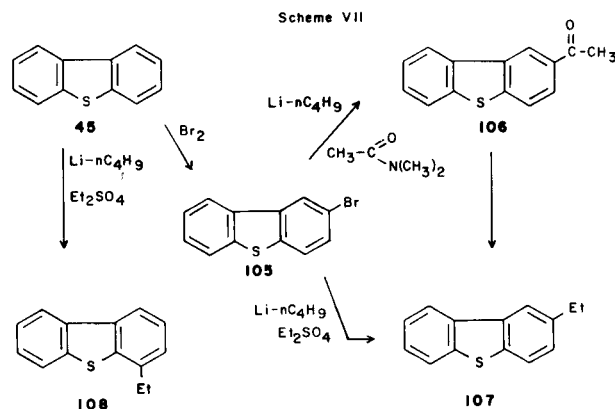
Alkylation of ethyl 2-oxocyclohexanecarboxylate (**98**) with ethyl iodide using sodium hydride as the catalyst gave ethyl 1-ethyl-2-oxocyclohexanecarboxylate (**99**) in 94% yield. Bromination of **99** at 0° gave ethyl 3-bromo-1-ethyl-2-oxocyclohexanecarboxylate (**100**) in 90% yield. When **100** was allowed to react with benzenethiol in the presence of ethanolic sodium ethoxide, ethyl 1-ethyl-2-oxo-3-phenylthiocyclohexanecarboxylate (**101**) was obtained in 70% yield. Cyclization of **101** (PPA) produced 1-ethyl-1,2,3,4-tetrahydrodibenzothiophene (**102**) in 55% yield.

Selenium aromatization of **102** gave 1-ethylidibenzothiophene (**104**) in 59% yield. Compound **104** was also prepared from 1-bromodibenzothiophene (**103**) [33] by first lithiation with *n*-butyllithium followed by treatment with diethyl sulfate producing **104** in 30% yield (Scheme VI). The nmr spectra and mass spectra of compound **104** obtained from **103** was identical to **104** obtained from **102**.

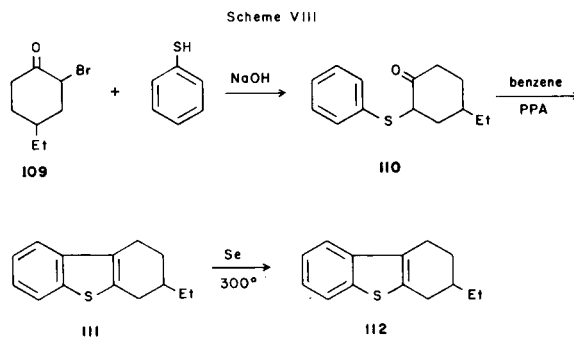


Dibenzothiophene (**45**) upon bromination gave 2-bromodibenzothiophene (**105**) [34] which upon lithiation (*n*-butyllithium) followed by reaction of the 2-lithiodibenzothiophene with *N,N*-dimethylacetamide produced 2-acetyldibenzothiophene (**106**) [26]. Compound **106** was allowed to reflux with hydrazine hydrate in diethylene glycol. The product was 2-ethylidibenzothiophene (**107**) in 69% yield. Compound **106** was also reduced to **107** in 58% yield with LAH. Compound **107** was also obtained from **105** by lithiation (*n*-butyllithium) followed by reaction with diethyl sulfate in 82% yield. Lithiation of dibenzothiophene occurs in the 4-position [33]. This lithio derivative reacted with di-

ethyl sulfate to give 4-ethylidibenzothiophene (**108**) in 86% yield (Scheme VII).



The reaction of 2-bromo-4-ethylcyclohexanone (**109**) with benzenethiol gave 4-ethyl-2-phenylthiocyclohexanone (**110**) in 80% yield which upon PPA cyclization produced 3-ethyl-1,2,3,4-tetrahydrodibenzothiophene (**111**) in 87% yield. Aromatization of **111** with selenium gave 3-ethylidibenzothiophene (**112**) in 60% yield. This reaction sequence is outlined in Scheme VIII.



## EXPERIMENTAL

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. The <sup>1</sup>H-nmr spectra were obtained on a Varian EM 360A spectrometer and JEOL FX-90Q spectrometer in deuteriochloroform. Chemical shifts are reported in δ units. The ir spectra were obtained on a Beckman Acculab 2 spectrometer. Mass spectra were obtained on a Hewlett-Packard model 590A mass spectrometer. Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona.

2-(*o*-Tolylthio)-4-methylcyclohexanone (**5**).

*o*-Methylbenzenethiol (**2**) (7.4 g, 59.6 mmoles) and 2.4 g of sodium hydroxide were dissolved in a solution of 15 ml of 95% ethanol and 15 ml of water. To this solution kept under a stream of nitrogen, 2-bromo-4-methylcyclohexanone (**1**) (12.5 g, 65.4 mmoles) dissolved in 95% ethanol (20 ml) was added dropwise. The reaction mixture was stirred at room temperature for 30 minutes and then refluxed for 4 hours. After cooling, 60 ml of water was added. The lower oily layer was removed and the aqueous phase was extracted with chloroform (3 × 40 ml). The oily layer was combined with the extracts, dried over anhydrous sodium sulfate and the volume reduced *in vacuo* giving 11.6 g (83%) of a yellow oil. An analytical sample was obtained by chromatography on a neutral alumina column using hexane:benzene (4:1) as the eluent affording a pale yellow oil; ir (neat): C=O 1690 cm<sup>-1</sup>; nmr (deuteriochloroform): δ 1.15 (s, CH-

$CH_3$ , 3H), 1.43-2.38 (m,  $-CH_2-CH(CH_3)-CH_2-$ , 5H), 2.28 (s, Ar- $CH_3$ , 3H), 2.51-3.21 (m,  $CH_2-CO$ , 2H), 3.62-3.90 (rough triplet of doublets, CO- $CH_2-S$ , 1H), 6.82-7.30 (m, 4H, ArH).

Anal. Calcd. for  $C_{14}H_{18}OS$ : C, 71.75; H, 7.74; S, 13.68. Found: C, 71.49; H, 7.60; S, 13.60.

#### 2-(*p*-Tolylthio)-4-methylcyclohexanone (6)

This compound was synthesized from *p*-methylbenzenethiol (3) (3.7 g, 29.8 mmoles), 1.2 g of sodium hydroxide and 2-bromo-4-cyclohexanone (6.3 g, 33 mmoles) in a manner similar to the preparation of compound 5 and 6.1 g (87%) of a yellow oil was obtained. An analytical sample was prepared by chromatography on a neutral alumina column using hexane:benzene (4:1) as the eluent giving a pale yellow oil; ir (neat):  $C=O$  1700  $cm^{-1}$ , nmr (deuteriochloroform):  $\delta$  1.15 (s,  $CH_3$ , 3H), 1.48-2.37 (m,  $-CH_2-CH(CH_3)-CH_2-$ , 5H), 2.15 (s, Ar- $CH_3$ , 3H), 2.48-3.20 (m,  $CH_2-CO$ , 2H), 3.58-3.89 (rough triplets of doublets, CO- $CH_2-S$ , 1H), 7.07 (dd,  $J = 1$ , 8 Hz, H-3, H-5, 2H, ArH), 7.18 (dd,  $J = 1$ , 8 Hz, H-2, H-6, 2H, ArH).

Anal. Calcd. for  $C_{14}H_{18}OS$ : C, 71.75; H, 7.74; S, 13.68. Found: C, 71.65; H, 7.58; S, 13.98.

#### 2-(Tolylthio)-4-methylcyclohexanone (7)

This compound was synthesized from *m*-methylbenzenethiol (4) (5.0 g, 40.2 mmoles), 1.7 g of sodium hydroxide and 2-bromo-4-methylcyclohexanone (1) (8.5 g, 44.3 mmoles) in a manner similar to the preparation of compound 5 and 8.8 g (85%) of a yellow oil was obtained. An analytical sample was prepared by chromatography on a neutral alumina column using hexane:benzene (4:1) as the eluent giving a pale yellow oil; ir (neat):  $C=O$  1685  $cm^{-1}$ .

Anal. Calcd. for  $C_{14}H_{18}OS$ : C, 71.75; H, 7.74; S, 13.68. Found: C, 72.05; H, 7.89; S, 14.01.

#### 3,6-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (8)

Compound 5 (3.0 g, 12.8 mmoles) was poured into a round bottom flask containing 30 g of polyphosphoric acid. This mixture was slowly heated in an oil bath with continuous stirring for 1.5 hours at 190-200°. After cooling, the mixture was poured into ice. The oily layer was separated and the aqueous phase extracted with chloroform (3  $\times$  50 ml). The oily layer and the extracts were combined, dried over anhydrous sodium sulfate and reduced *in vacuo* yielding 1.9 g (69%) of a yellow oil. The compound was used in the next reaction without further purification.

#### 3,8-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (9)

Compound 9 was synthesized from compound 6 (4.0 g, 17.1 mmoles) and 40 g of polyphosphoric acid in a manner similar to the preparation of compound 8 and 2.7 g (67%) of a yellow oil was obtained. The compound was used in the next reaction without further purification.

#### 3,7-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (10) and 3,9-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (11)

Compounds 10 and 11 were synthesized from compound 7 (4.0 g, 17.1 mmoles) and 40 g of polyphosphoric acid in a manner similar to the preparation of compound 8 and 2.5 g (69%) of a dark oil was obtained. The mixture of crude 10 and 11 was used in the next reaction without further separation or purification.

#### 3,6-Dimethyldibenzothiophene (12)

Compound 8 (1.4 g, 6.5 mmoles) and powdered selenium (1.5 g, 0.019 g-atom) was heated to 300° in a flask fitted with a condenser. A rubber hose was fitted to the top of the condenser which led to a series of two traps. The second trap was filled with copper sulfate solution to prevent the hydrogen selenide gas that evolved from the reaction from escaping. The first trap was left empty to prevent any copper sulfate solution from backing up into the reaction mixture. The heating was continued until the evolution of hydrogen selenide gas ceased (approximately 8 hours). After cooling, 95% ethanol (45 ml) was added and the mixture refluxed for 30 minutes. The hot alcoholic solution was filtered, to remove the selenium metal, treated with activated carbon and reduced *in vacuo* affording 1.03 g (75%) of pale yellow oil. This oil was chromatographed on an

alumina column using hexane as the eluent giving colorless crystals, mp 65°; nmr (deuteriochloroform):  $\delta$  2.49 (s,  $CH_3$ -3, 3H), 2.59 (s,  $CH_3$ -6, 3H), 7.12-7.37 (m, H-7, H-8, 2H, ArH), 7.43 (d,  $J = 8$  Hz, H-2, 1H, ArH), 7.68 (s, H-4, 1H, ArH), 7.82-8.03 (m, H-9, 1H, ArH), 8.05 (d,  $J = 8$  Hz, H-1, 1H, ArH); ms:  $m/e$  214 ( $M^+ + 2$ , 6), 213 ( $M^+ + 1$ , 18), 212 ( $M^+$ , 100), 211 (49).

Anal. Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 78.95; H, 5.83; S, 15.29.

#### 2,7-Dimethyldibenzothiophene (13)

This compound was prepared from compound 9 (2.0 g, 9.2 mmoles) and powdered selenium (2.0 g, 0.025 g-atom) in a manner similar to the preparation of compound 12 and 1.6 g (81%) of a yellow oil was obtained. The oil was chromatographed on an alumina column using hexane as the eluent giving colorless crystals, mp 36°; nmr (deuteriochloroform):  $\delta$  2.42 (s,  $CH_3$ -2 and  $CH_3$ -7, 6H), 7.27 (d,  $J = 8$  Hz, H-3 and H-8, 2H, ArH), 7.76 (s, H-6, 1H, ArH), 7.83 (d,  $J = 8$  Hz, H-4, 1H, ArH), 8.08 (s, H-1, 1H, ArH), 8.16 (d,  $J = 8$  Hz, H-9, 1H, ArH); ms:  $m/e$  214 ( $M^+ + 2$ , 5), 213 ( $M^+ + 1$ , 16), 212 ( $M^+$ , 100), 211 (56).

Anal. Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.27; H, 5.65; S, 15.25.

#### 3,7-Dimethyldibenzothiophene (14) and 1,7-Dimethyldibenzothiophene (15)

Compounds 14 and 15 were prepared from the mixture 10 and 11 (2.0 g, 9.3 mmoles) and powdered selenium (2.0 g, 0.025 g-atom) in a manner similar to the preparation of compound 12 and 1.5 g (77%) of pale yellow oil was obtained. The oil was chromatographed on neutral alumina using hexane as the eluent and again with basic alumina and pentane as the eluent giving 0.80 g (41%) of colorless crystals of compound 14, mp 150-151° (lit mp 150-152° [21]) and 0.61 g (31%) of colorless crystals of compound 15. Compound 14 has nmr (deuteriochloroform):  $\delta$  2.49 (s, 2  $\times$   $CH_3$ , 6H), 7.22 (dd,  $J = 1$ , 8 Hz, H-2, H-8, 2H, ArH), 7.61 (s, H-4, H-6, 2H, ArH), 7.92 (d,  $J = 8$  Hz, H-1, H-9, 2H, ArH); ms:  $m/e$  214 ( $M^+ + 2$ , 6), 213 ( $M^+ + 1$ , 18), 212 ( $M^+$ , 100), 211 (47), 204 (33).

Anal. Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.43; H, 5.84; S, 14.87.

#### 1,7-Dimethyldibenzothiophene (15)

1-Chloromethyl-7-methyldibenzothiophene (38) (1.0 g, 4.1 mmoles) was dissolved in 60 ml of absolute ether and lithium aluminum hydride (0.5 g, 13.3 mmoles) was carefully added. The mixture was stirred at room temperature under a stream of nitrogen for 3.5 hours and then quenched by cautiously adding 10 ml of water and enough 20% hydrochloric acid to dissolve the inorganic salts. The mixture was poured into ice-water and extracted twice with 50 ml of benzene. The extracts were washed successively with water and saturated sodium bicarbonate solution and then dried over anhydrous sodium sulfate and evaporated. The residue was chromatographed on a column of silica gel using hexane as the eluent giving colorless crystals (89%), mp 53°; nmr (deuteriochloroform):  $\delta$  2.44 (s,  $CH_3$ -7, 3H), 2.85 (s,  $CH_3$ -1, 3H), 7.18 (d,  $J = 8$  Hz, H-8, 1H, ArH), 7.06-7.39 (m, H-2, H-3, 2H, ArH), 7.58 (dd,  $J = 1$ , 8 Hz, H-4, 1H, ArH), 7.60 (s, H-6, 1H, ArH), 8.13 (d,  $J = 8$  Hz, H-9, 1H, ArH); ms:  $m/e$  213 ( $M^+ + 1$ , 17), 212 ( $M^+$ , 100), 211 (50).

Anal. Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 14.87. Found: C, 79.11; H, 5.58; S, 14.62.

#### 2-Allyl-4-methylbenzo[*b*]thiophene (20)

4-Methylbenzo[*b*]thiophene (16) [22] (33.3 g, 225 mmoles) in 400 ml of dry ether was placed in a 3 neck 1000 ml flask under a nitrogen atmosphere. The solution was cooled to  $-70^\circ$  and *n*-butyllithium (168 ml, 267 mmoles) was added dropwise. The solution was allowed to stir for 30 minutes at  $-70^\circ$  to  $-50^\circ$  and an additional 90 minutes at room temperature. After cooling the reaction mixture to  $-70^\circ$ , a solution of allyl bromide (21.4 ml, 247 mmoles) in 50 ml of dry ether was added dropwise and the stirring was continued at room temperature overnight. The reaction mixture was poured into ice-water and acidified with enough 20% hydrochloric acid to dissolve the inorganic salts. The organic layer was separated and the aqueous layer extracted with ether (2  $\times$  200 ml). The

organic layer and extracts were combined, washed with water and saturated sodium bicarbonate, dried over anhydrous sodium sulfate and evaporated *in vacuo* affording a brown oil. Distillation at 79-83° (0.2 mm Hg) gave 37.22 g (88%) of orange oil; nmr (deuteriochloroform):  $\delta$  2.55 (s,  $\text{CH}_3$ , 3H), 3.57 (d, J = 6 Hz,  $-\text{CH}_2-\text{CH}=\text{, 2H}$ ), 4.99 (s,  $\text{H}_2$  at  $=\text{CH}_2$ , 1H), 5.20 (d, J = 6 Hz,  $\text{H}_1$  of  $=\text{CH}_2$ , 1H), 5.59-6.32 (m,  $-\text{CH}=\text{CH}_2$ , 1H), 6.85 (s, H-3, 1H, ArH), 6.87-7.30 (m, H-5, H-6, 7-H, 3H, ArH); ms: m/e 188 ( $\text{M}^+$ , 100), 187 (43), 147 (53).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{12}\text{S}$ : C, 76.55; H, 6.42; S, 17.03. Found: C, 76.38; H, 6.36; S, 17.41.

#### 2-Allyl-5-methylbenzo[b]thiophene (21).

This compound was prepared from compound 17 [22] (33.3 g, 22.5 mmoles), *n*-butyllithium (168 ml, 267 mmoles) and allyl bromide (21 ml, 247 mmoles) in a manner similar to the preparation of compound 20. Distillation gave 34.28 g (81%) of orange oil, bp 91-96° at 0.2 mm Hg; nmr (deuteriochloroform):  $\delta$  2.39 (s,  $\text{CH}_3$ , 3H), 3.57 (d, J = 6 Hz,  $-\text{CH}_2-\text{CH}=\text{, 2H}$ ), 5.01 (s,  $\text{H}_2$  of  $=\text{CH}_2$ , 1H), 5.23 (d, J = 6 Hz,  $\text{H}_1$  of  $=\text{CH}_2$ , 1H), 5.62-6.38 (m,  $-\text{CH}=\text{CH}_2$ , 1H), 6.87 (s, H-3, 1H, ArH), 6.99-7.22 (m, H-5, 1H, ArH), 7.44 (d, J = 6 Hz, H-7, 1H, ArH), 7.64 (s, H-4, 1H, ArH); ms: m/e 189 ( $\text{M}^+ + 1$ , 16), 188 ( $\text{M}^+$ , 100), 187 (44), 161 (49).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{12}\text{S}$ : C, 76.55; H, 6.42; S, 17.03. Found: C, 76.35; H, 6.56; S, 17.25.

#### 2-Allyl-6-methylbenzo[b]thiophene (22).

Compound 22 was obtained from 6-methylbenzo[b]thiophene (18) (62 g, 418 mmoles), *n*-butyllithium (343 ml, 544 mmoles) and allyl bromide (40 ml, 460 mmoles) in a manner similar to the preparation of compound 20. Distillation gave an orange oil (64.55 g, 82%), bp 79-83° at 0.2 mm Hg; nmr (deuteriochloroform):  $\delta$  2.38 (s,  $\text{CH}_3$ , 3H), 3.56 (d, J = 6 Hz,  $\text{CH}_2-\text{CH}=\text{, 2H}$ ), 4.99 (s,  $\text{H}_2$  of  $=\text{CH}_2$ , 1H), 5.22 (d, J = 6 Hz,  $\text{H}_1$  of  $=\text{CH}_2$ , 1H), 5.53-6.32 (m,  $-\text{CH}=\text{, 1H}$ ), 6.87 (s, H-3, 1H, ArH), 7.00 (dd, J = 1, 6 Hz, H-5 1H, ArH), 7.38 (s, H-7, 1H, ArH), 7.49 (dd, J = 1, 6 Hz, H-4, 1H, ArH); ms: m/e 188 ( $\text{M}^+$ , 100), 187 (42), 173 (27), 161 (46).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{12}\text{S}$ : C, 76.55; H, 6.42; S, 17.03. Found: C, 76.80; H, 6.74; S, 17.46.

#### 2-Allyl-7-methylbenzo[b]thiophene (23).

This compound was obtained from 7-methylbenzo[b]thiophene (19) [22] (62 g, 418 mmoles), *n*-butyllithium (343 ml, 534 mmoles) and allyl bromide (40 ml, 460 mmoles) in a manner similar to the preparation of compound 20. Distillation gave an orange oil (59 g, 75%), bp 74-78° at 0.2 mm Hg; nmr (deuteriochloroform):  $\delta$  7.40 (s,  $\text{CH}_3$ , 3H), 3.62 (d, J = 6 Hz,  $-\text{CH}_2-\text{CH}=\text{, 2H}$ ), 5.03 (s,  $\text{H}_2$  of  $\text{CH}_2=\text{, 1H}$ ), 5.24 (d, J = 6 Hz,  $\text{H}_1$  of  $\text{CH}_2=\text{, 1H}$ ), 5.68-6.48 (m,  $-\text{CH}=\text{, 1H}$ ), 7.03 (s, H-3, 1H, ArH), 6.98-7.27 (m, H-5, H-6, 2H, ArH), 7.59 (d, J = 6 Hz, H-4, 1H, ArH); ms: m/e 188 ( $\text{M}^+$ , 100), 187 (48).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{12}\text{S}$ : C, 76.55; H, 6.42; S, 17.03. Found: C, 76.59; H, 6.50; S, 17.23.

#### Ethyl 9-Methyldibenzothiophene-1-carboxylate (24).

Anhydrous stannic chloride (18.5 ml, 159 mmoles) was added to a stirred solution of 2-allyl-4-methylbenzo[b]thiophene (20) (26 g, 138 mmoles) and methylene chloride (350 ml) at  $-70^\circ$  to  $-60^\circ$ . To the resultant reaction mixture was added ethyl dichloroethoxyacetate [25] (27.8 g, 138 mmoles) and stirring was continued for 30 minutes. The mixture was then allowed to warm to room temperature and the stirring was continued overnight. The reaction mixture was poured into 400 ml of ice-water, the organic layer was separated and the aqueous phase extracted with methylene chloride (3  $\times$  100 ml). The combined extracts were washed with aqueous sodium bicarbonate and then water, dried over sodium sulfate and the volume reduced *in vacuo* affording an oil. The residue was chromatographed on a neutral alumina column, using hexane:benzene (3:1) as the eluent giving 28.4 g (76%) of pale yellow oil; nmr (deuteriochloroform):  $\delta$  1.35 (t, J = 8 Hz,  $\text{CH}_2-\text{CH}_3$ , 3H), 2.63 (s,  $\text{CH}_3$ , 3H), 4.28 (q, J = 8 Hz,  $-\text{CH}_2-\text{CH}_3$ , 2H), 7.00-7.52 (m, H-2, H-3, H-7, H-8, 4H, ArH), 7.86 (dd, J = 1, 8 Hz, H-4, H-6, 2H, ArH); ms: m/e 270 ( $\text{M}^+$ , 100), 225 (58).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{10}\text{O}_2\text{S}$ : C, 71.08; H, 5.22; S, 11.80. Found: C,

71.30; H, 5.49; S, 11.95.

#### Ethyl 8-Methyldibenzothiophene-1-carboxylate (25).

This compound was prepared from compound 21 (36.0 g, 191 mmoles), methylene chloride (400 ml), anhydrous stannic chloride (24 ml, 210 mmoles) and ethyl dichloroethoxyacetate [25] (40.2 g, 200 mmoles) in a manner similar to the preparation of compound 24. An analytical sample was obtained by chromatography on a neutral alumina column, using hexane:benzene (3:1) as the eluent giving 40.8 g (79%) of pale yellow oil; nmr (deuteriochloroform):  $\delta$  1.48 (t, J = 8 Hz,  $\text{CH}_2-\text{CH}_3$ , 3H), 2.51 (s,  $\text{CH}_3$ , 3H), 4.50 (q, J = 8 Hz,  $\text{CH}_2-\text{CH}_3$ , 2H), 7.02-7.90 (m, H-2, H-3, H-4, H-5, H-6, 5H, ArH), 8.14 (s, H-9, 1H, ArH); ms: m/e 271 ( $\text{M}^+ + 1$ , 18), 270 ( $\text{M}^+$ , 100), 225 (47).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}$ : C, 71.08; H, 5.22; S, 11.86. Found: C, 71.21; H, 5.30; S, 12.10.

#### Ethyl 7-Methyldibenzothiophene-1-carboxylate (26).

Compound 26 was obtained from compound 22 (42.6 g, 226 mmoles), methylene chloride (450 ml), anhydrous stannic chloride (30.3 ml, 263 mmoles) and ethyl dichloroethoxyacetate [25] (45.5 g, 226 mmoles) in a manner similar to the preparation of compound 24. The yield was 75% (pale yellow oil); nmr (deuteriochloroform):  $\delta$  1.30 (t, J = 8 Hz,  $\text{CH}_2-\text{CH}_3$ , 3H), 2.44 (s,  $\text{CH}_3$ , 3H), 4.25 (q, J = 8 Hz,  $-\text{CH}_2-\text{CH}_3$ , 2H), 6.91 (m, H-2, H-3, H-6, 3H, ArH), 7.72 (dd, J = 1, 8 Hz, H-4, 1H, ArH), 7.90 (s, H-6, 1H, ArH), 8.12 (d, J = 8 Hz, H-9, 1H, ArH); ms: m/e 270 ( $\text{M}^+$ , 100), 225 (61).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}$ : C, 71.08; H, 5.22; S, 11.86. Found: C, 71.24; H, 5.11; S, 12.20.

#### Ethyl 6-Methyldibenzothiophene-1-carboxylate (27).

Compound 27 was prepared in the same manner as compound 24 and 73% of colorless oil was obtained; nmr (deuteriochloroform):  $\delta$  1.32 (t, J = 8 Hz,  $\text{CH}_2-\text{CH}_3$ , 3H), 2.52 (s,  $\text{CH}_3$ , 3H), 4.25 (q, J = 8 Hz,  $-\text{CH}_2-\text{CH}_3$ , 2H), 7.48-7.90 (m, H-2, H-3, H-7, H-8, 4H, ArH), 8.04 (dd, J = 1, 8 Hz, H-4, 1H, ArH), 8.24 (d, J = 8 Hz, H-9, 1H, ArH); ms: m/e 270 ( $\text{M}^+$ , 100), 225 (74), 215 (48), 197 (56).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}$ : C, 71.08; H, 5.22; S, 11.86. Found: C, 71.40; H, 5.49; S, 10.92.

#### 9-Methyldibenzothiophene-1-carboxylic Acid (28).

Compound 24 (39.0 g, 141 mmoles) was dissolved in a mixture of 200 ml of methanol and 200 ml of 15% aqueous sodium hydroxide. The reaction mixture was refluxed for 6 hours, poured in ice after cooling and acidified with concentrated hydrochloric acid affording colorless crystals. The crystals were collected by filtration and recrystallized in ethanol giving 31.5 g (90%) of colorless crystals, mp 200-201°; nmr (deuteriochloroform):  $\delta$  2.66 (s,  $\text{CH}_3$ , 3H), 7.03-7.67 (m, H-2, H-3, H-7, H-8, 4H, ArH), 7.81 (m, H-4, H-6, 2H, ArH); ms: m/e 243 ( $\text{M}^+ + 1$ , 15), 242 ( $\text{M}^+$ , 100), 197 (26).

Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}$ : C, 69.40; H, 4.16; S, 13.23. Found: C, 69.52; H, 4.23; S, 13.42.

#### 8-Methyldibenzothiophene-1-carboxylic Acid (29).

Compound 29 was prepared in a similar manner to compound 28, and colorless crystals (89%) were obtained, mp 198-200°; nmr (deuteriochloroform):  $\delta$  2.51 (s,  $\text{CH}_3$ , 3H), 7.04-8.01 (m, H-2, H-3, H-4, H-6, H-7, 5H, ArH), 8.30 (s, H-9, 1H, ArH); ms: m/e 244 ( $\text{M}^+ + 2$ , 6), 243 ( $\text{M}^+ + 1$ , 15), 242 ( $\text{M}^+$ , 100), 197 (23), 196 (22).

Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}$ : C, 69.40; H, 4.16; S, 13.23. Found: C, 69.52; H, 4.00; S, 12.82.

#### 7-Methyldibenzothiophene-1-carboxylic Acid (30).

Compound 30 was prepared in a similar manner to compound 28 and colorless crystals (92%) were obtained, mp 192-194°; nmr (deuteriochloroform):  $\delta$  2.50 (s,  $\text{CH}_3$ , 3H), 7.08-7.71 (m, H-2, H-3, H-8, 3H, ArH), 7.72 (dd, J = 1, 8 Hz, H-4, 1H, ArH), 7.96 (s, H-6, 1H, ArH), 8.43 (d, J = 8 Hz, H-9, 1H, ArH); ms: m/e 242 ( $\text{M}^+$ , 100), 197 (25), 196 (13).

Anal. Calcd. for  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{S}$ : C, 69.40; H, 4.16; S, 13.23. Found: C, 69.68; H, 4.27; S, 13.10.

6-Methylthiophene-1-carboxylic Acid (**31**).

Compound **31** was prepared in a similar manner to compound **28** and colorless crystals (88%) were obtained, mp 189-191°; nmr (deuteriochloroform):  $\delta$  2.56 (s,  $CH_3$ , 3H), 7.22-7.84 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 8.06 (dd,  $J = 1, 8$  Hz, H-4, 1H, *ArH*), 8.23 (dd,  $J = 1, 8$  Hz, H-9, 1H, *ArH*); ms:  $m/e$  242 ( $M^+$ , 100), 215 (92), 197 (24).

*Anal.* Calcd. for  $C_{14}H_{10}O_2S$ : C, 69.40; H, 4.16; S, 13.23. Found: C, 69.29; H, 4.10; S, 13.40.

1-Hydroxymethyl-9-methyldibenzothiophene (**32**).

Lithium aluminum hydride (8 g) was added to a suspension of 9-methyldibenzothiophene-1-carboxylic acid (**28**) (17.0 g, 70.2 mmoles) and absolute ether (500 ml). The reaction mixture was stirred at room temperature for 3.5 hours under nitrogen and then quenched by cautiously adding 40 ml of water and enough 20% hydrochloric acid to dissolve the inorganic salts. The mixture was poured into ice-water and extracted twice with 150 ml of benzene. The extracts were washed successively with water and saturated sodium bicarbonate solution and then dried over sodium sulfate and evaporated. The residue was recrystallized in methanol affording pale yellow crystals (15.2 g, 95%), mp 130-131°; nmr (deuteriochloroform):  $\delta$  2.01 (bs, *OH*, 1H), 2.58 (s,  $CH_3$ , 3H), 5.27 (s,  $CH_2$ , 2H), 7.04-7.52 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.58-7.89 (m, H-4, H-6, 2H, *ArH*); ms:  $m/e$  229 ( $M^+$  + 1, 15), 228 ( $M^+$ , 100), 199 (39).

*Anal.* Calcd. for  $C_{14}H_{12}OS$ : C, 73.65; H, 5.30; S, 14.04. Found: C, 73.23; H, 5.35; S, 14.10.

1-Hydroxymethyl-8-methyldibenzothiophene (**33**).

This compound was prepared in a similar manner to compound **32** and pale yellow crystals (93%) were obtained, mp 139-140°; nmr (deuteriochloroform):  $\delta$  1.81 (bs, *OH*, 1H), 2.53 (s,  $CH_3$ , 3H), 5.20 (s,  $CH_2$ -OH, 2H), 7.11-7.50 (m, H-2, H-3, H-7, 3H, *ArH*), 7.58-7.88 (m, H-4, H-6, 2H, *ArH*), 8.12 (s, H-9, 1H, *ArH*); ms:  $m/e$  230 ( $M^+$  + 2, 5), 229 ( $M^+$  + 1, 15), 228 ( $M^+$ , 100), 199 (34), 184 (35).

*Anal.* Calcd. for  $C_{14}H_{12}OS$ : C, 73.65; H, 5.30; S, 14.04. Found: C, 73.42; H, 5.39; S, 13.91.

1-Hydroxymethyl-7-methyldibenzothiophene (**34**).

Compound **34** was prepared in a similar manner to compound **32** and pale yellow crystals were obtained (95%), mp 128-129°; nmr (deuteriochloroform):  $\delta$  1.79 (bs, *OH*, 1H), 2.49 (s,  $CH_3$ , 3H), 5.18 (s,  $CH_2$ , 2H), 7.08-7.47 (m, H-2, H-3, H-8, 3H, *ArH*), 7.51-7.83 (m, H-4, H-6, 2H, *ArH*), 8.21 (dd,  $J = 1, 8$  Hz, H-9, 1H, *ArH*); ms:  $m/e$  229 ( $M^+$  + 1, 15), 228 ( $M^+$ , 100), 211 (31), 199 (52), 184 (53).

*Anal.* Calcd. for  $C_{14}H_{12}OS$ : C, 73.65; H, 5.30; S, 14.04. Found: C, 73.46; H, 5.48; S, 13.89.

1-Hydroxymethyl-6-methyldibenzothiophene (**35**).

This compound was prepared in a similar manner to compound **32** and pale yellow crystals (91%) were obtained, mp 123-124°; nmr (deuteriochloroform):  $\delta$  2.18 (bs, *OH*, 1H), 2.56 (s,  $CH_3$ , 3H), 5.13 (s,  $CH_2$ , 2H), 7.03-7.51 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.78 (dd,  $J = 1, 8$  Hz, H-4, 1H, *ArH*), 8.13 (dd,  $J = 1, 8$  Hz, H-9, 1H, *ArH*); ms:  $m/e$  229 ( $M^+$  + 1, 15), 228 ( $M^+$ , 100).

*Anal.* Calcd. for  $C_{14}H_{12}OS$ : C, 73.65; H, 5.30; S, 14.04. Found: C, 73.40; H, 5.15; S, 14.30.

1-Chloromethyl-9-methyldibenzothiophene (**36**).

A mixture of compound **32** (13.5 g, 59 mmoles), 28 ml of thionyl chloride and 300 ml of dry benzene was refluxed for 2.5 hours. After removal of benzene and excess of thionyl chloride *in vacuo*, the residue was recrystallized from ethanol to give 12.84 g (85%) of yellowish needles, mp 100-101°; nmr (deuteriochloroform):  $\delta$  2.61 (s,  $CH_3$ , 3H), 5.28 (s,  $CH_2$ , 2H), 7.09-7.51 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.76 (dd,  $J = 1, 8$  Hz, H-4, H-6, 2H, *ArH*); ms:  $m/e$  248 ( $M^+$  + 1, 20), 247 ( $M^+$ , 50), 211 (100).

*Anal.* Calcd. for  $C_{14}H_{11}ClS$ : C, 68.15; H, 4.49; S, 12.99. Found: C, 68.52; H, 4.32; S, 12.68.

1-Chloromethyl-8-methyldibenzothiophene (**37**).

This compound was prepared in a similar manner to compound **36** and pale yellow needles were obtained (88%) mp 106-107°; nmr (deuteriochloroform):  $\delta$  2.56 (s,  $CH_3$ , 3H), 5.12 (s,  $CH_2Cl$ , 2H), 7.08-7.50 (m, H-2, H-3, H-7, 3H, *ArH*), 7.75 (dd,  $J = 1, 8$  Hz, H-4, H-6, 2H, *ArH*), 8.19 (s, H-9, 1H, *ArH*); ms:  $m/e$  249 ( $M^+$  + 2, 3), 248 ( $M^+$  + 1, 23), 247 ( $M^+$ , 63), 211 (100).

*Anal.* Calcd. for  $C_{14}H_{11}ClS$ : C, 68.15; H, 4.49; S, 12.99. Found: C, 68.45; H, 4.60; S, 13.09.

1-Chloromethyl-7-methyldibenzothiophene (**38**).

Compound **38** was prepared in a manner similar to compound **36** and pale yellow needles were obtained (87%), mp 98°; nmr (deuteriochloroform):  $\delta$  2.50 (s,  $CH_3$ , 3H), 5.20 (s,  $CH_2Cl$ , 2H), 7.09-7.50 (m, H-2, H-3, H-8, 3H, *ArH*), 7.53-7.85 (m, H-4, H-6, 2H, *ArH*), 8.20 (dd,  $J = 1, 8$  Hz, H-9, 1H, *ArH*); ms:  $m/e$  248 ( $M^+$  + 1, 21), 247 ( $M^+$ , 64), 211 (100).

*Anal.* Calcd. for  $C_{14}H_{11}ClS$ : C, 68.15; H, 4.49; S, 12.99. Found: C, 67.92; H, 4.62; S, 13.25.

1-Chloromethyl-6-methyldibenzothiophene (**39**).

This compound was prepared in a similar manner to compound **36** and pale yellow needles were obtained (90%), mp 148-150°; nmr (deuteriochloroform):  $\delta$  2.60 (s,  $CH_3$ , 3H), 5.13 (s,  $CH_2Cl$ , 2H), 7.09-7.61 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.83 (dd,  $J = 1, 8$  Hz, H-4, H-6, 2H, *ArH*), 8.23 (dd,  $J = 1, 8$  Hz, H-9, 1H, *ArH*); ms:  $m/e$  248 ( $M^+$  + 1, 20), 247 ( $M^+$ , 65), 211 (100).

*Anal.* Calcd. for  $C_{14}H_{11}ClS$ : C, 68.15; H, 4.49; S, 12.99. Found: C, 68.45; H, 4.60; S, 13.09.

1,9-Dimethyldibenzothiophene (**40**).

Compound **40** was prepared in a similar manner to compound **15** and colorless crystals were obtained (88%), mp 89-90°; nmr (deuteriochloroform):  $\delta$  2.89 (s,  $2 \times CH_3$ , 6H), 7.03-7.39 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.68 (dd,  $J = 1, 8$  Hz, H-4, H-6, 2H, *ArH*); ms:  $m/e$  212 ( $M^+$ , 100).

*Anal.* Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.30; H, 5.89; S, 15.40.

1,8-Dimethyldibenzothiophene (**41**).

Compound **41** was prepared in a similar manner to compound **15** and colorless crystals (90%) were obtained, mp 73-74°; nmr (deuteriochloroform):  $\delta$  2.39 (s,  $CH_3$ -8, 3H), 2.71 (s,  $CH_3$ -1, 3H), 7.02 (dd,  $J = 1, 8$  Hz, H-2, H-3, 2H, *ArH*), 7.20 (dd,  $J = 1, 8$  Hz, H-7, 1H, *ArH*), 7.26-7.70 (m, H-4, H-6, 2H, *ArH*), 7.88 (s, H-9, 1H, *ArH*); ms:  $m/e$  212 ( $M^+$ , 100).

*Anal.* Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.02; H, 5.80; S, 15.03.

1,6-Dimethyldibenzothiophene (**42**).

This compound was prepared in a similar manner to compound **15** and colorless crystals (88%) were obtained, mp 74-75°; nmr (deuteriochloroform):  $\delta$  2.51 (s,  $CH_3$ -6, 3H), 2.82 (s,  $CH_3$ -1, 3H), 6.90-7.43 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.60 (dd,  $J = 1, 8$  Hz, H-4, 1H, *ArH*), 8.06 (dd,  $J = 1, 8$  Hz, H-9, 1H, *ArH*); ms:  $m/e$  214 ( $M^+$  + 2, 6), 213 ( $M^+$  + 1, 18), 212 ( $M^+$ , 100), 211 (44).

*Anal.* Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.19; H, 5.96; S, 15.00.

2-(*p*-Tolylthio)-3-methylcyclohexanone (**46**) and 2-(*p*-Tolylthio)-5-methylcyclohexanone (**47**).

Compounds **46** and **47** were prepared from a mixture of compounds **44** and **45** (11.0 g, 57.6 mmoles), 4-methylbenzenethiol (6.5 g, 52.3 mmoles), sodium hydroxide (2.5 g), 12.0 ml of 95% ethanol and 12.0 ml of water in a manner similar to the preparation of compound **5** and a yellow oil was obtained (9.8 g, 80%). The mixture was crude **46** and **47** was used in the next reaction without further separation or purification.

4,8-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**48**) and 2,8-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**49**).

Compounds **48** and **49** were prepared from the crude mixture of **46** and **47** (8.5 g, 36.3 mmoles) and polyphosphoric acid (70 g) in a manner

similar to the preparation of compound **8**. Purification was *via* neutral alumina column chromatography, using hexane:benzene (4:1) as the eluent, affording a yellow oil (5.18 g, 66%). Compounds **48** and **49** were not separated at this stage and were used in the next reaction.

#### 2,8-Dimethyldibenzothiophene (**51**).

*n*-Butyllithium (5.0 g of 1.7 *M* solution) was slowly added to a suspension of 2,8-dibromodibenzothiophene (**53**) [26] (5.0 g, 14.6 mmoles) and dry ether (150 ml). The reaction mixture was refluxed for 12 hours and dimethylsulfate (2.0 g, 16 mmoles) was slowly added. Reflux was continued for another five hours. After cooling, the reaction mixture was poured in ice-water, the organic layer was separated and the aqueous layer extracted twice with 100 ml of benzene. The combined extracts were washed with water, dried over anhydrous sodium sulfate and evaporated. The crude residue was chromatographed on a neutral alumina column using hexane and then benzene affording colorless crystals (0.6 g, 28%) of compound **51**, mp 113° (lit mp 112-113° [26]) and starting material (3.6 g, 72%); nmr literature [26] (the nmr reported by Campaigne and Ashby has 7.21 (dd,  $J_{3,4} = 7$  Hz,  $J_{3,1} = 2$  Hz, H-3,6. This should have been H-3,7); ms: *m/e* 214 ( $M^+ + 2$ , 5), 213 ( $M^+ + 1$ , 16), 212 ( $M^+$ , 100), 211 (51).

#### 2,6-Dimethyldibenzothiophene (**50**) and 2,8-Dimethyldibenzothiophene (**51**).

Compounds **50** and **51** were prepared from the mixture of **48** and **49** (5.0 g, 23.1 mmoles) and powdered selenium (5.4 g, 0.07 g-atom) in a manner similar to the preparation of compound **12**. The residue was chromatographed on a neutral alumina column using hexane as the eluent and again with a basic alumina column using pentane as the eluent affording 2,8-dimethyldibenzothiophene (**51**) [26] (1.67 g, 34%) as colorless crystals, mp 113° and 2,6-dimethyldibenzothiophene (**50**) (1.52 g, 31%) as colorless crystals, mp 99-100°. The physical properties and spectral data of compound **51** were identical to compound **51** obtained unambiguously from **53**. Compound **50** had nmr (deuteriochloroform):  $\delta$  2.44 (s,  $CH_3$ -2, 3H), 2.52 (s,  $CH_3$ -6, 3H), 6.92-7.40 (m, H-3, H-7, H-8, 3H, *ArH*), 7.59 (d,  $J = 8$  Hz, H-4, 1H, *ArH*) 7.73 (s, H-1, 1H, *ArH*), 7.60-7.91 (m, H-9, 1H, *ArH*); ms: *m/e* 214 ( $M^+ + 2$ , 6), 213 ( $M^+ + 1$ , 18), 212 ( $M^+$ , 100), 211 (48).

*Anal.* Calcd. for  $C_{14}H_{12}S$  for compound **50**: C, 79.20; H, 5.70; S, 15.10. Found: C, 79.14; H, 5.43; S, 14.69.

#### 2-(*o*-Tolylthio)-3-methylcyclohexanone (**55**) and 2-(*o*-Tolylthio)-5-methylcyclohexanone (**56**).

Compounds **55** and **56** were prepared from a mixture of compounds **44** and **45** (11.0 g, 57.6 mmoles), *o*-methylbenzenethiol (**54**) (6.5 g, 52.3 mmoles), sodium hydroxide (2.5 g), 12.0 ml of 95% ethanol and 12.0 ml of water in a manner similar to the preparation of compound **5** and a yellow oil was obtained (9.5 g, 78%). The mixture of crude **55** and **56** was used in the next reaction without further separation or purification.

#### 4,6-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**57**) and 2,6-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**58**).

Compounds **57** and **58** were prepared from the crude mixture **55** and **56** (8.5 g, 36.3 mmoles) and polyphosphoric acid (70 g) in a manner similar to the preparation of compound **8**. Purification was accomplished *via* neutral alumina column chromatography, using hexane:benzene (4:1) as the eluent, affording a yellow oil (5.38 g, 69%). Compounds **57** and **58** were not separated, and were used in the next reaction.

#### 4,6-Dimethyldibenzothiophene (**59**) and 2,6-Dimethyldibenzothiophene (**50**).

Compounds **59** and **50** were obtained from the mixture of compounds **57** and **58** (5.0 g, 23.1 mmoles) and powdered selenium (5.4 g, 0.068 g-atom) in a manner similar to the preparation of compound **12**. The residue was chromatographed on a neutral alumina column using hexane as the eluent and again on a basic alumina column using pentane as the eluent affording 4,6-dimethyldibenzothiophene (**59**) (1.72 g, 35%) as colorless crystals, mp 153-154° (lit mp 154-155° [27,28]) and 2,6-dimethyldibenzothiophene (**50**) (1.42 g, 29%) as colorless crystals. The physical pro-

erties and spectral data of compound **50** were identical to compound **50** obtained from the mixture **48** and **49**. Compound **59** has nmr (deuteriochloroform):  $\delta$  2.59 (s,  $2 \times CH_3$ , 6H), 7.09-7.51 (m, H-2, H-3, H-7, H-8, 4H, *ArH*), 7.90 (dd,  $J = 1, 8$  Hz, H-1, H-9, 2H, *ArH*); ms: *m/e* 214 ( $M^+ + 2$ , 5), 213 ( $M^+ + 1$ , 17), 212 ( $M^+$ , 100), 211 (42).

*Anal.* Calcd. for compound **59**,  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.05; H, 5.53; S, 14.60.

#### 2,3-Dimethylphenyl Ethyl Xanthate (**70**).

Concentrated hydrochloric acid (46 ml) was added to a stirred mixture of crushed ice (100 g) and 2,3-dimethylaniline (**60**) (30 g, 0.248 mole). The reaction mixture was maintained at 0° during diazotization of the amine by the dropwise addition of a solution of sodium nitrite (18 g, 0.261 mole) in 30 ml of water. The stirring was continued for 30 minutes maintaining the temperature at 0°.

Technical potassium ethyl xanthate (60 g, 0.374 mole) in 75 ml of water was heated to 40° in a one liter three neck flask equipped with a double walled condenser, a dropping funnel and an efficient stirrer. The cold diazonium solution was added dropwise with stirring at such a rate that the temperature did not exceed 45°. The cooled mixture was extracted with three 150 ml portions of ether. The combined extracts were washed with 50 ml of 10% sodium carbonate solution, several times with water and finally dried over anhydrous sodium sulfate. The volume was reduced *in vacuo* yielding 55.0 g (98%) of yellow oil; nmr (deuteriochloroform):  $\delta$  1.21 (t,  $J = 8$  Hz,  $-CH_2CH_3$ , 3H), 2.20 (s,  $CH_3$ -3, 3H), 2.30 (s,  $CH_3$ -2, 3H), 4.54 (q,  $J = 8$  Hz,  $O-CH_2$ , 2H), 6.89-7.41 (m, 3H, *ArH*) [29].

#### 2,4-Dimethyl Ethyl Xanthate (**71**).

Compound **71** was prepared from compound **61** in a manner similar to the preparation of compound **70**. The yield obtained was 97% (yellow oil); nmr (deuteriochloroform):  $\delta$  1.29 (t,  $J = 8$  Hz,  $-CH_2-CH_3$ , 3H), 2.30 (s,  $CH_3$ -2, 3H), 2.34 (s,  $CH_3$ -4, 3H), 4.49 (q,  $J = 8$  Hz,  $O-CH_2$ , 2H), 6.94 (d,  $J = 8$  Hz, H-5, 1H, *ArH*), 7.07 (s, H-3, 1H, *ArH*), 7.31 (d,  $J = 8$  Hz, H-6, 1H, *ArH*) [29].

#### 2,5-Dimethylphenyl Ethyl Xanthate (**72**).

Compound **72** was prepared from compound **62** in a manner similar to the preparation of compound **70**. A yellow oil was obtained (98%); nmr (deuteriochloroform):  $\delta$  1.39 (t,  $J = 8$  Hz,  $-CH_2-CH_3$ , 3H), 2.29 (s,  $CH_3$ -5, 3H), 3.34 (s,  $CH_3$ -2, 3H), 4.51 (q,  $J = 8$  Hz,  $O-CH_2$ , 2H), 6.87-7.31 (m, 3H, *ArH*) [29].

#### 3,5-Dimethylphenyl Ethyl Xanthate (**73**).

Compound **73** was prepared from compound **63** in a manner similar to the preparation of compound **70**. A yellow oil was obtained (92%); nmr (deuteriochloroform):  $\delta$  1.36 (t,  $J = 8$  Hz,  $-CH_2-CH_3$ , 3H), 2.28 (s,  $2 \times CH_3$ , 6H), 4.58 (q,  $J = 8$  Hz,  $O-CH_2$ , 2H), 7.06 (s, H-2, H-6, 2H, *ArH*), 7.14 (s, H-4, 1H, *ArH*) [29].

#### 3,4-Dimethylphenyl Ethyl Xanthate (**74**).

This compound was prepared from compound **64** in a manner similar to the preparation of compound **70**. A yellow oil was obtained (97%); nmr (deuteriochloroform):  $\delta$  1.23 (t,  $J = 8$  Hz,  $-CH_2-CH_3$ , 3H), 2.20 (bs,  $2 \times CH_3$ , 6H), 4.48 (q,  $J = 8$  Hz,  $O-CH_2$ , 2H), 6.90-7.32 (m, 3H, *ArH*) [29].

#### 2,3-Dimethylbenzenethiol (**75**).

Anhydrous 2,3-dimethylphenyl ethyl xanthate (**70**) (26 g, 0.115 mole) and absolute ether (500 ml) were placed in a three-neck one liter flask with a double walled condenser, a dropping funnel and an efficient stirrer. Solid, technical grade lithium aluminum hydride (8.7 g, 0.230 mole) was added slowly under a stream of nitrogen, with stirring at such a rate that the ether refluxed gently without external cooling. The stirring was continued for three hours and then quenched by adding 40 ml of water from a dropping funnel to hydrolyze the reaction mixture followed by addition of enough 20% hydrochloric acid to dissolve the inorganic salts. The mixture was poured into ice-water, the organic layer was separated and the aqueous layer extracted three times with 150 ml of ether. The organic layer and extracts were combined, washed with saturated sodium



bicarbonate and several times with water, dried over anhydrous sodium sulfate and evaporated *in vacuo* affording a pale yellow oil (14.9 g, 94%) [29]. This compound was used in the next reaction without further purification.

#### 2,4-Dimethylbenzenethiol (**76**).

Compound **76** was prepared from compound **71** in a manner similar to the preparation of compound **75**. A yellow oil was obtained in 93% yield [29]. This compound was used in the next reaction without further purification.

#### 2,5-Dimethylbenzenethiol (**77**).

This compound was prepared from compound **72** in a manner similar to the preparation of compound **75**. A yellow oil was obtained in 90% yield [29]. This compound was used in the next reaction without further purification.

#### 3,5-Dimethylbenzenethiol (**78**).

This compound was prepared from compound **73** in a manner similar to the preparation of compound **75**. A yellow oil was obtained in 92% yield [29]. This compound was used in the next reaction without further purification.

#### 3,4-Dimethylbenzenethiol (**79**).

Compound **79** was prepared from compound **74** in a manner similar to the preparation of compound **75**. A yellow oil was obtained in 95% yield [29]. This compound was used in the next reaction without further purification.

#### 2-(2,3-Dimethylphenylthio)cyclohexanone (**81**).

This compound was prepared from **75** (15.0 g, 0.109 mole), sodium hydroxide (6.5 g) and freshly prepared 2-bromocyclohexanone (**80**) [31] (21.2 g, 0.120 mole) in a manner similar to the preparation of compound **5** and 21.7 g (85%) of pale yellow crystals was obtained, mp 47-48°; nmr (deuteriochloroform):  $\delta$  1.70-2.35 (m,  $3 \times \text{CH}_2$ , 6H), 2.24 (s,  $\text{CH}_3$ -3, 3H), 2.33 (s,  $\text{CH}_3$ -2, 3H), 2.55-3.23 (m,  $\text{CH}_2$ -CO-, 2H), 3.62-3.93 (rough triplet of doublets, CO-CH-S, 1H), 6.78-7.34 (m, 3H, ArH); ms: m/e 234 ( $\text{M}^+$ , 62), 138 (100).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{18}\text{OS}$ : C, 71.75; H, 7.74; S, 13.68. Found: C, 71.89; H, 7.93; S, 13.29.

#### 2-(2,4-Dimethylphenylthio)cyclohexanone (**82**).

This compound was prepared in a similar manner to compound **81** and a pale yellow oil (84%) was obtained; nmr (deuteriochloroform):  $\delta$  1.39-2.20 (m,  $3 \times \text{CH}_2$ , 6H), 2.23 (s,  $\text{CH}_3$ -4, 3H), 2.37 (s,  $\text{CH}_3$ -2, 3H), 2.62-3.19 (m,  $\text{CH}_2$ -CO-, 2H), 3.59-3.78 (m, rough triplet of doublets, CO-CH-S), 6.96 (s, H-3, 1H, ArH), 7.22 (dd,  $J = 1, 8$  Hz, H-5, H-6, 2H, ArH); ms: m/e 236 ( $\text{M}^+ + 2, 4$ ), 235 ( $\text{M}^+ + 1, 11$ ), 234 ( $\text{M}^+$ , 67), 138 (100).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{18}\text{OS}$ : C, 71.75; H, 7.74; S, 13.68. Found: C, 72.03; H, 7.95; S, 13.40.

#### 2-(2,5-Dimethylphenylthio)cyclohexanone (**83**).

This compound was prepared according to Fujiwara, Acton and Goodman's procedure [20] and the mp obtained was 47-49° (lit mp 44-48° [20]); ms: m/e 234 ( $\text{M}^+$ , 90), 138 (100).

#### 2-(3,5-Dimethylphenylthio)cyclohexanone (**84**).

This compound was prepared in a similar manner to compound **81** and pale yellow crystals (82%) were obtained, mp 50-51°; nmr (deuteriochloroform):  $\delta$  1.36-2.50 (m,  $3 \times \text{CH}_2$ , 6H), 2.34 (s,  $2 \times \text{CH}_3$ , 6H), 2.70-3.19 (m,  $\text{CH}_2$ -CO-, 2H), 3.62-3.90 (rough triplet of doublets, CO-CH-S), 6.88 (d,  $J = 8$  Hz, H-4, 1H, ArH), 6.92 (s, H-2, H-6, 2H, ArH); ms: m/e 234 ( $\text{M}^+$ , 58), 138 (100).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{18}\text{OS}$ : C, 71.75; H, 7.74; S, 13.68. Found: C, 71.62; H, 7.85; S, 13.79.

#### 2-(3,4-Dimethylphenylthio)cyclohexanone (**85**).

This compound was obtained in a similar manner to the preparation of

compound **81** and pale yellow crystals were obtained (81%), mp 46-49°; nmr (deuteriochloroform):  $\delta$  1.40-2.40 (m,  $3 \times \text{CH}_2$ , 6H), 2.20 (bs,  $2 \times \text{CH}_3$ , 6H), 2.55-3.08 (m, - $\text{CH}_2$ -CO-, 2H), 3.52-3.87 (rough triplets of doublets, CO-CH-S, 1H), 7.08 (s, H-6, 1H, ArH), 7.18 (d,  $J = 3$  Hz, H-2, H-5, 2H, ArH); ms: m/e 234 ( $\text{M}^+$ , 72), 138 (100).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{18}\text{OS}$ : C, 71.75; H, 7.74; S, 13.68. Found: C, 71.40; H, 7.61; S, 13.83.

#### 6,7-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**86**).

This compound was prepared from compound **81** (10.0 g, 46 mmoles) and polyphosphoric acid (10 g) in a manner similar to the preparation of compound **8** and a pale yellow oil (84%) was obtained; nmr (deuteriochloroform):  $\delta$  1.60-2.05 (m,  $\text{CH}_2$ -2,  $\text{CH}_2$ -3, 4H), 2.34 (s,  $\text{CH}_3$ -6, 3H), 2.38 (s,  $\text{CH}_3$ -7, 3H), 2.48-3.04 (m,  $\text{CH}_2$ -1,  $\text{CH}_2$ -4, 4H), 6.93 (d,  $J = 4$  Hz, H-8, 1H, ArH), 7.06 (d,  $J = 4$  Hz, H-9, 1H, ArH); ms: m/e 216 ( $\text{M}^+$ , 100), 188 (89).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{16}\text{S}$ : C, 77.72; H, 7.45; S, 14.82. Found: C, 77.69; H, 7.43; S, 14.98.

#### 6,8-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**87**).

Compound **87** was prepared from compound **82** (6.0 g, 25.6 mmoles) and polyphosphoric acid (8 g) in a manner similar to the preparation of compound **8** and a pale yellow oil (80%) was obtained; nmr (deuteriochloroform):  $\delta$  1.53-2.03 (m,  $\text{CH}_2$ -2,  $\text{CH}_2$ -3, 4H), 2.27 (s,  $\text{CH}_3$ -8, 3H), 2.44 (s,  $\text{CH}_3$ -6, 3H), 2.51-3.23 (m,  $\text{CH}_2$ -1,  $\text{CH}_2$ -4, 4H), 6.89 (s, H-7, 1H, ArH), 7.18 (s, H-9, 1H, ArH); ms: m/e 216 ( $\text{M}^+$ , 100), 188 (88), 138 (94).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{16}\text{S}$ : C, 77.72; H, 7.45; S, 14.82. Found: C, 77.98; H, 7.62; S, 15.13.

#### 6,9-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**88**).

This compound was prepared according to Fujiwara, Acton and Goodman's method [20] and pale yellow crystals were obtained, mp 34-35°; nmr: lit [20]; ms: m/e 216 ( $\text{M}^+$ , 100), 188 (93).

#### 7,9-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**89**).

Compound **89** was prepared from compound **84** (7.0 g, 29.9 mmoles) and polyphosphoric acid (8 g) in a manner similar to the preparation of compound **8** and yellow crystals were obtained (78%), mp 37-38°; nmr (deuteriochloroform):  $\delta$  1.58-2.09 (m,  $\text{CH}_2$ -2,  $\text{CH}_2$ -3, 4H), 2.20 (s,  $\text{CH}_2$ -3, 2H), 2.51 (s,  $\text{CH}_2$ -1, 2H), 2.54-3.09 (m,  $\text{CH}_2$ -1,  $\text{CH}_2$ -4, 4H), 6.73 (s, H-8, 1H, ArH), 6.92 (s, H-6, 1H, ArH); ms: m/e 216 ( $\text{M}^+$ , 100), 188 (89).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{16}\text{S}$ : C, 77.72; H, 7.45; S, 14.82. Found: C, 77.85; H, 7.62; S, 14.73.

#### 8,9-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**90**) and 7,8-Dimethyl-1,2,3,4-tetrahydrodibenzothiophene (**91**).

Compounds **90** and **91** were obtained from compound **85** (8.5 g, 36.3 mmoles) and polyphosphoric acid (10 g) in a manner similar to the preparation of compound **8**. Purification of the mixture **90** and **91** was done by chromatography on neutral alumina using hexane:benzene (4:1) as the eluent. The combined yield was 89%. The mixture was used in the next reaction without purification.

#### 3,4-Dimethyldibenzothiophene (**92**).

Compound **92** was prepared from compound **86** (2.0 g, 9.2 mmoles) and powdered selenium (5.0 g) in a similar manner to the preparation of compound **12**. An analytical sample was prepared by chromatography on a neutral alumina column using hexane as the eluent, affording colorless crystal (1.24 g, 63%), mp 60-61°; nmr (deuteriochloroform):  $\delta$  2.32 (s,  $\text{CH}_3$ -3, 3H), 2.37 (s,  $\text{CH}_3$ -4, 3H), 7.19 (dd,  $J = 2, 8$  Hz, H-7, H-8, 2H, ArH), 7.38 (d,  $J = 2$  Hz, H-2, 1H, ArH), 7.68 (dd,  $J = 2, 8$  Hz, H-6, 1H, ArH), 7.69-8.08 (m, H-1, H-9, 2H, ArH); ms: m/e 213 ( $\text{M}^+ + 1, 16$ ), 212 ( $\text{M}^+$ , 100), 211 (24), 197 (53).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{12}\text{S}$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 78.91; H, 6.05; S, 14.89.

#### 2,4-Dimethyldibenzothiophene (**93**).

This compound was prepared in a similar manner to compound **12** and a colorless oil (75%) was obtained, (lit mp 10° [32]); nmr lit [32]; ms: m/e

213 ( $M^+ + 1$ , 16), 212 ( $M^+$ , 100).

1,4-Dimethyldibenzothiophene (94).

This compound was prepared from compound **88** in a similar manner to the preparation of compound **12** and a colorless oil (75%) was obtained; bp 154-156° (0.1 mm Hg), (lit bp 137-139°, 0.07 mm Hg [20]); nmr lit [20]; ms: m/e 213 ( $M^+ + 1$ , 16), 212 ( $M^+$ , 100).

1,3-Dimethyldibenzothiophene (95).

This compound was prepared from compound **89** in a manner similar to the preparation of compound **12** and colorless crystals were obtained (71%), mp 110° (lit mp 110° [32]); nmr lit [32]; ms: m/e 213 ( $M^+ + 1$ , 17), 212 ( $M^+$ , 100), 211 (24), 197 (59).

1,2-Dimethyldibenzothiophene (96) and 2,3-Dimethyldibenzothiophene (97).

Compounds **96** and **97** were obtained from the mixture of **90** and **91** (6.5 g, 30.0 mmoles) and powdered selenium (6.0 g), in a manner similar to the preparation of compound **12**. The residue was chromatographed on neutral alumina using hexane as an eluent affording pure **96** as the first fraction. The second fraction consisted of a mixture of **96** and **97** which was chromatographed again on basic alumina using pentane as the eluent. The first fraction was again **97** and the combined yield of **97** was 1.98 g (32%). The second fraction consisted of pure **96** (colorless crystals) obtained in 28% yield (1.71 g).

Compound 96.

This compound had a mp 55-56°; nmr (deuteriochloroform):  $\delta$  2.38 (s,  $CH_3$ -2, 3H), 2.85 (s,  $CH_3$ -1, 3H), 7.00-7.75 (m, H-3, H-4, H-6, H-7, H-8, 5H, ArH), 7.80 (d, J = 8 Hz, H-9, 1H, ArH); ms: m/e 213 ( $M^+ + 1$ , 17), 212 ( $M^+$ , 100), 197 (52).

Anal. Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.35; H, 5.41; S, 15.39.

Compound 97.

This compound had a mp 69-70°; nmr (deuteriochloroform):  $\delta$  2.21 (s,  $CH_3$ -3, 3H), 2.30 (s,  $CH_3$ -2, 3H), 6.99-7.48 (m, H-7, H-8, 2H, ArH), 7.51 (s, H-4, 1H, ArH), 7.49-7.53 (m, H-6, 1H, ArH), 7.82 (s, H-1, 1H, ArH), 7.80-7.87 (m, H-9, 1H, ArH); ms: m/e 213 ( $M^+ + 1$ , 15), 212 ( $M^+$ , 100), 197 (55).

Anal. Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.11; H, 5.67; S, 15.30.

Ethyl 1-Ethyl-2-oxocyclohexanecarboxylate (99).

Sodium hydride (50% dispersion in mineral oil, 5.5 g, 0.23 mole) was washed twice with 50 ml of dry hexane and suspended in 200 ml of tetrahydrofuran. The slurry was cooled to 0° under a stream of nitrogen and ethyl 2-oxocyclohexanecarboxylate (14.5 g, 85.2 mmoles) (**98**) was slowly added with continuous stirring. After the addition the solution was stirred at room temperature for one hour, cooled to 0° and ethyl iodide (19.0 g, 0.122 mole) was added dropwise. The resulting mixture was stirred at room temperature overnight and then carefully quenched by adding 150 ml of water. The organic layer was separated and the aqueous layer extracted three times with ether. The combined extracts were dried over anhydrous sodium sulfate and evaporated giving a yellow oil (15.9 g, 94%). The compound was used in the next reaction without further purification.

Ethyl 3-Bromo-1-ethyl-2-oxocyclohexanecarboxylate (100).

Bromine (15.0 g, 93.9 mmoles) was added dropwise into a mixture of compound **99** (16.89 g, 85.2 mmoles) and 20 ml of water at 0°. After the addition the reaction mixture was stirred at room temperature for four hours and then poured into 200 ml of ice-water. The organic layer was separated and the aqueous layer was extracted twice with chloroform. The organic layer and extracts were combined, dried over anhydrous sodium sulfate and evaporated to give a brown oil (21.25 g, 90%). The compound was used in the next reaction without further purification.

Ethyl 1-Ethyl-2-oxo-3-phenylthiocyclohexanecarboxylate (101).

Benzenethiol (11.0 g, 99.9 mmoles) was added to a suspension of sodium metal (2.5 g, 0.109 g-atom) in 150 ml of 100% ethanol at 0° under a stream of nitrogen. The reaction mixture was stirred at room temperature for one hour, and cooled to 0°. A solution of compound **100** (30.44 g, 109.8 mmoles) in 50 ml of 100% ethanol was added carefully and the reaction mixture was refluxed for two hours. After cooling, the mixture was poured into 500 ml of water, the organic layer separated and the aqueous layer extracted twice with 100 ml of chloroform. The combined extracts were dried over anhydrous sodium sulfate and evaporated. The residue was chromatographed on a neutral alumina column using hexane:benzene (3:1) as the eluent giving a pale yellow oil (21.42 g, 70%); nmr deuteriochloroform:  $\delta$  0.80 (t, J = 8 Hz, C- $CH_2$ - $CH_3$ , 3H), 1.20 (t, J = 8 Hz, O- $CH_2$ - $CH_3$ , 3H), 1.40-2.60 (m, 3  $\times$   $CH_2$ , 6H), 3.48-3.84 (rough triplet of doublets, CO- $CH$ -S, 1H), 3.50 (q, C- $CH_2$ - $CH_3$ , 2H), 4.12 (q, O- $CH_2$ - $CH_3$ , 2H), 7.00-7.50 (m, 5H, ArH); ms: m/e 306 ( $M^+$ , 44), 233 (47), 204 (100).

Anal. Calcd. for  $C_{17}H_{22}O_3S$ : C, 66.64; H, 7.24; S, 10.46. Found: C, 66.50; H, 7.50; S, 10.20.

1-Ethyl-1,2,3,4-tetrahydrodibenzothiophene (102).

Compound **101** (18 g, 58.7 mmoles) and polyphosphoric acid (30 g) were placed into a 300 ml round bottom flask and heated to 145-155° for 3 hours with continuous stirring. After cooling, the reaction mixture was extracted twice with benzene by refluxing it with 100 ml of dry benzene for ten minutes. Both times the extraction was allowed to cool and the benzene was decanted. The combined extracts were filtered and evaporated. The residue was chromatographed on neutral alumina using hexane:benzene (4:1) as the eluent affording a yellow oil (7.0 g, 55%); ms: m/e 216 ( $M^+$ , 100), 187 (57).

Anal. Calcd. for  $C_{14}H_{16}S$ : C, 77.72; H, 7.45; S, 14.82. Found: C, 77.45; H, 7.50; S, 15.10.

1-Ethylidibenzothiophene (104).

Method A.

Compound **104** was prepared from compound **102** (4.0 g, 18.5 mmoles) and powdered selenium (5.0 g) in a similar manner to compound **12** and a colorless oil (2.3 g, 59%) was obtained.

Method B.

1-Bromodibenzothiophene (**103**) (0.6 g, 2.3 mmoles) [33] in 30 ml of dry ether was placed in a 100 ml three neck flask with an addition funnel, thermometer and a tube as an inlet for dry nitrogen. This solution was then cooled to 0° and *n*-butyllithium (1.7 M in hexane, 2.0 ml) was added dropwise. After the addition the mixture was stirred for two hours at room temperature. The mixture was cooled to 0° and diethyl sulfate (2.0 ml) was added. After addition the solution was refluxed for five hours, cooled and poured into 100 ml of 10% hydrochloric acid solution. The organic layer was separated and the aqueous layer extracted twice with 50 ml of chloroform. The combined extracts were dried over anhydrous sodium sulfate and evaporated. The residue was chromatographed on neutral alumina using hexane as the eluent giving a colorless oil (0.011 g, 30%); nmr (deuteriochloroform):  $\delta$  1.30 (t, J = 8 Hz,  $CH_2$ - $CH_3$ , 3H), 4.19 (q, J = 8 Hz,  $CH_2$ - $CH_3$ , 2H), 7.09-8.40 (m, H-2, H-3, H-7, H-8, 4H, ArH), 7.52-7.82 (m, H-4, H-6, 2H, ArH), 8.08 (dd, J = 1, 8 Hz, H-9, 1H, ArH); ms: m/e 212 ( $M^+$ , 50), 197 (100).

Anal. Calcd. for  $C_{14}H_{12}S$ : C, 79.20; H, 5.70; S, 15.10. Found: C, 79.35; H, 5.80; S, 14.93.

2-Acetyldibenzothiophene (106).

This compound was prepared similarly to the Campaigne and Ashby procedure [26] and colorless crystals were obtained, mp 110-111° (lit mp 92-98° [26] and 111° [33]).

2-Ethylidibenzothiophene (107).

Method A.

This compound was prepared from 2-bromodibenzothiophene (**105**) (5.0 g, 0.019 mole) [34] in a similar manner to the preparation of compound **104** (Method B) and a colorless oil (3.3 g, 82%) was obtained.

## Method B.

Compound **106** (1.0 g, 4.4 mmoles), diethylene glycol (10 ml) and hydrazine hydrate (4 ml) was stirred and refluxed for 2.5 hours. At that point the condenser was removed and the water produced by the reaction was allowed to evaporate. After refluxing without a condenser for 35 minutes, the condenser was replaced and the reaction mixture was allowed to reflux for another 3 hours. The temperature reached 160°. After cooling potassium hydroxide pellets (0.8 g) were added and the mixture refluxed for 1.5 hours. The reaction mixture was poured into ice-water after cooling, extracted with ether twice (70 ml), dried over anhydrous sodium sulfate and evaporated *in vacuo*. The residue was chromatographed on neutral alumina using hexane as the eluent affording a colorless oil (0.65 g, 69%).

## Method C.

Lithium aluminum hydride (0.8 g) was slowly added *via* a spatula to a suspension of compound **106** (2.1 g, 9.3 mmoles), aluminum chloride (2.66 g, 19.9 mmoles) and absolute ether (100 ml). The reaction mixture was refluxed for 3.5 hours maintaining the ether level by occasional addition of absolute ether. The ether layer was washed successively with water and dilute alkali solution and evaporated. The residue was chromatographed on a silica gel column using hexane as the eluent affording a colorless oil (1.15 g, 58%); nmr (deuteriochloroform):  $\delta$  1.30 (t, J = 8 Hz, CH<sub>2</sub>-CH<sub>3</sub>, 3H), 2.78 (q, J = 8 Hz, CH<sub>2</sub>-CH<sub>3</sub>, 2H), 7.08-7.50 (m, H-3, H-7, H-8, 3H, ArH), 7.58-7.92 (m, H-4, H-6, 2H, ArH), 7.98 (s, H-1, 1H, ArH), 7.96-8.22 (m, H-9, 1H, ArH), ms: m/e 212 (M<sup>+</sup>, 52), 197 (100), 184 (31).

Anal. Calcd. for C<sub>14</sub>H<sub>12</sub>S: C, 79.20; H, 5.70; S, 15.10. Found: C, 79.67; H, 5.67; S, 14.62.

4-Ethyldibenzothiophene (**108**).

This compound was prepared from 4-lithiodibenzothiophene [33] in a similar manner to the method B preparation of compound **104** and a colorless oil (86%) was obtained; nmr (deuteriochloroform):  $\delta$  1.13 (t, J = 8 Hz, CH<sub>2</sub>-CH<sub>3</sub>, 3H), 2.60 (q, J = 8 Hz, CH<sub>2</sub>-CH<sub>3</sub>, 2H), 6.90-7.29 (m, H-2, H-3, H-7, H-8, 4H, ArH), 7.47 (d, J = 2 Hz, H-6, 1H, ArH), 7.50-7.89 (m, H-1, H-9, 2H, ArH); ms: m/e 212 (M<sup>+</sup>, 51), 197 (76), 184 (100).

Anal. Calcd. for C<sub>14</sub>H<sub>12</sub>S: C, 79.20; H, 5.70; S, 15.10. Found: C, 79.34; H, 5.86; S, 15.16.

4-Ethyl-2-phenylthiocyclohexanone (**110**).

This compound was prepared from compound **109** in a similar manner to the preparation of compound **5** and a pale yellow oil was obtained (80%); ms: m/e 234 (M<sup>+</sup>, 56), 110 (100).

Anal. Calcd. for C<sub>14</sub>H<sub>18</sub>OS: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.69; H, 7.81; S, 13.82.

3-Ethyl-1,2,3,4-tetrahydridibenzothiophene (**111**).

Compound **111** was prepared from compound **110** in a similar manner to the preparation of compound **8** and a pale yellow oil was obtained (87%); nmr (deuteriochloroform):  $\delta$  0.87 (t, J = 8 Hz, CH<sub>2</sub>-CH<sub>3</sub>, 3H), 1.25-2.18 (m, CH<sub>2</sub>-2 and CH, 3H), 2.25-3.22 (m, CH<sub>2</sub>-CH<sub>3</sub> and CH<sub>2</sub>-1, CH<sub>2</sub>-4, 6H), 7.06-7.80 (m, 4H, ArH); ms: m/e 216 (M<sup>+</sup>, 100), 187 (54).

Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>S: C, 77.72; H, 7.45; S, 14.82. Found: C, 77.39; H, 7.30; S, 14.62.

3-Ethyldibenzothiophene (**112**).

Compound **112** was prepared from compound **111** in a similar manner to the preparation of compound **12** and a colorless oil (60%) was obtained; nmr (deuteriochloroform):  $\delta$  2.31 (t, J = 8 Hz, CH<sub>2</sub>-CH<sub>3</sub>, 3H), 3.19 (q, J = 8 Hz, CH<sub>2</sub>-CH<sub>3</sub>, 2H), 7.06-7.48 (m, H-2, H-7, H-8, 3H, ArH), 7.63 (s, H-4, 1H, ArH), 7.54-7.78 (m, H-6, 1H, ArH), 7.87-8.21 (m, H-1, H-9, 2H, ArH); ms: m/e 212 (M<sup>+</sup>, 52), 197 (100).

Anal. Calcd. for C<sub>14</sub>H<sub>12</sub>S: C, 79.20; H, 5.70; S, 15.10. Found: C, 79.50; H, 5.82; S, 14.80.

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