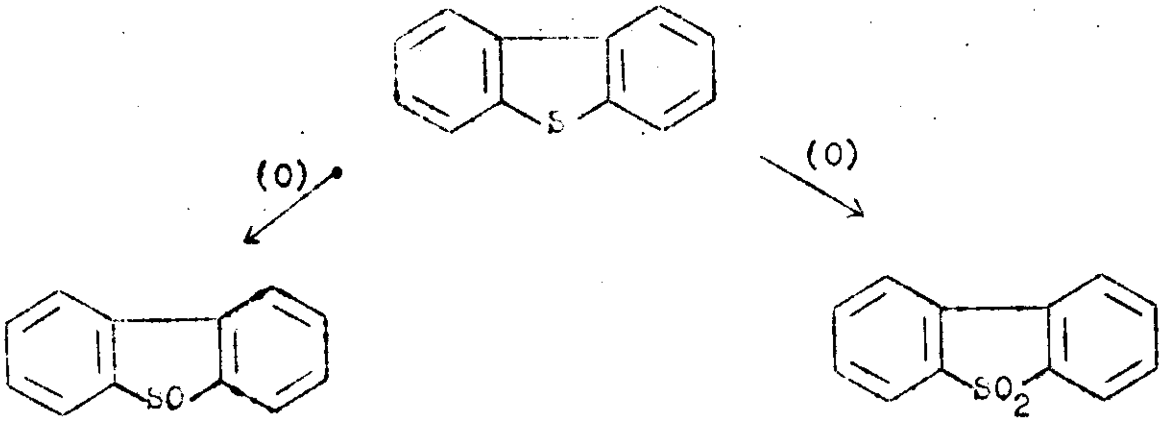
II- INTRODUCTION

CHEMISTRY OF DIBENZOTHIOPHENES

I) Naturally Occuring Dibenzothiophenes (in crude oil and coal tar):

Analysis of four crude oils has indicated the presence of approximately 200 individual sulfur compounds split into 13 main classes, one of which represents dibenzothiophene and its derivatives. For example, both dibenzothiophene and tetrahydrodibenzothiophene derivatives are thought to be present in a high-boiling (225 - 400°) Wasson, Texas, crude oil distillate (1). Distillation of the heavy fractions of Lacq petroleum has yielded 23 fractions (2) from which dibenzothiophene itself, together with 4-methyldibenzothiophene and 3 other derivatives, possibly 2-methyl-, 4,6-dimethyl-and a trimethyldibenzothiophene, have been isolated. Kuwait distillates, which are known to have an unusually high sulfur content, contain considerable amounts of alkyldibenzothiophenes, including 4,6-dimethyldibenzothiophene and other tetramethyldibenzothiophene derivatives (3,4). Dibenzothiophene derivatives have also been shown to be present in both light (5) and heavy (6) catalytic cycle oils and Middle East Tubricating oils (7) and dibenzothiophene and alkyl derivatives including 4,6-dimethyldibenzothiophene have been detected in anthracene oil (8,9). Technical phenanthrene obtained from coal tar is known (10) to be contaminated with up to 6 - 8 % dibenzothiophene as well as with the more readily detected anthracene.

Separation of dibenzothiophene derivatives from petroleum oil fractions has been achieved by integrated approaches (11, 12) in which fractionating processes(1,2,4) such as isothermal distillation, vacuum fractionation, and molecular distillation have been combined with spectroscopic methods including mass spectrometry (1,2,12,13) and NMR spectroscopy (11). Dibenzothiophenes have also been concentrated in sharp chromatographic fractions obtained, for example, by alumina gel percolation (5), and have been detected by gas chromatography (6,8,14). Gas chromatography has also been used to separate mixtures of sulfones (15) including that of dibenzothiophene. Mixtures of dibenzothiophene and either phenanthrene or dibenzofuran have been successfully separated (16) by TLC using petroleum ether and alumina-impregnated glass paper. Separation of mixtures of heterocycles including dibenzothiophene, its sulfoxide and sulfone has been achieved using either silica gel or alumina (17) in hexane or carbon tetrachloride.



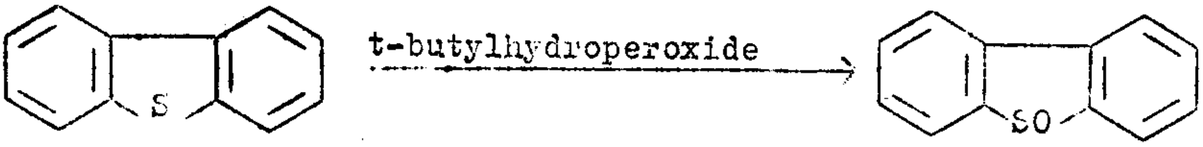
I

II

Sergienko *et al* (22) was found that, the use of an excess of peracetic acid in petroleum ether at 106° gave, after 45 min, a 97 % yield of the sulfone (II), while termination of the reaction after 5 min. gave the sulfoxide (II) (52 %).

Ford and Young (23) have investigated the kinetics of the oxidation of dibenzothiophene by peracetic acid using acetic acid-benzene as solvent in the temperature rang 15-60° and in this work obtained yields of sulfoxide of 94 %.

Oxidation of dibenzothiophene with t-butylhydroperoxide proceeded slowly and its was only possible to measure reaction rates in the concentration range 0.3 - 0.6 mole/liter in acetic acid at 60°. The reaction did not proceed beyond the sulfoxide (I) and it was obtained in 35 % yield (33).



I (35 %)

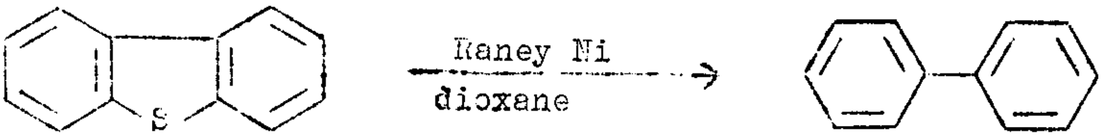
The kinetics of the oxidation of dibenzothiophene with perbenzoic acid in 1:1 dioxane-water has been studied in the range 0 - 40°, in this system the sulfoxide (I) was oxidised approximately 10 times more slowly than the parent compound (24).

The mechanism of formation of the sulfoxide (I) from dibenzothiophene with chlorine in acetic acid has been studied (25). Sodium acetate showed a strong accelerating effect and the results suggested the formation of a dibenzothiophene-chlorine adduct which then decomposed giving the sulfoxide (I).

Despite the fact that dibenzothiophene can be readily oxidized with peracetic acid, it is generally resistant to milder oxidative conditions. It is, for example, stable to heating in an inert solvent at 150° in the presence of bronze and oxygen, conditions under which both biphenyl sulfide and dibenzyl sulfide gave insoluble precipitates (26).

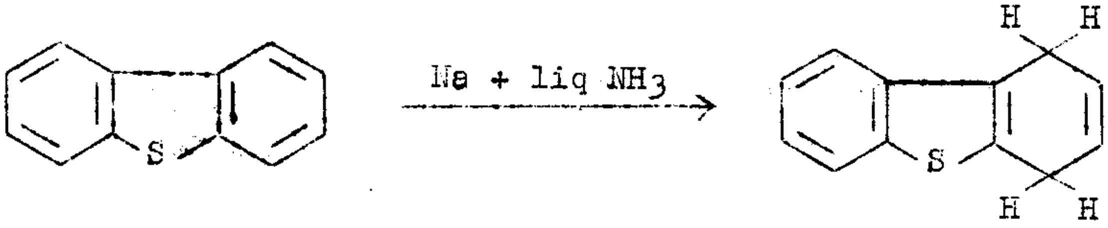
C) Reduction and Desulfurization:

Raney nickel in ethanol (3,27) or dioxane (22) readily desulfurizes dibenzothiophene and many of its derivatives. Quantitative yields of biphenyl (III) are obtained from dibenzothiophene using W7 Raney nickel (28), while Raney cobalt is less effective (29). Treatment of 2-bromodibenzothiophene with Raney nickel gave biphenyl as the only product (30).



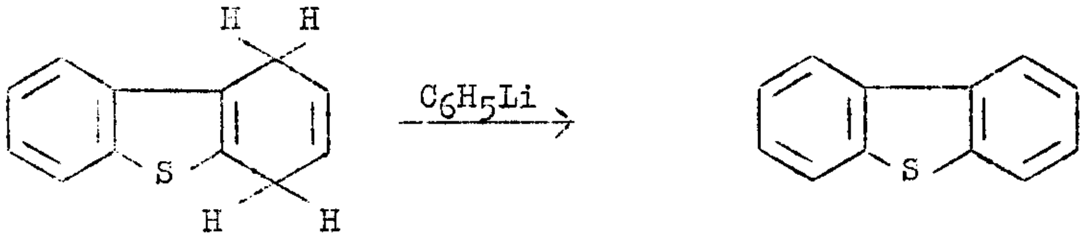
(III)

Reduction of dibenzothiophene with sodium in liquid ammonia has been shown to be sensitive to the experimental methods employed; however, the major product is usually 1,4-dihydrodibenzothiophene (IV) (31-33).



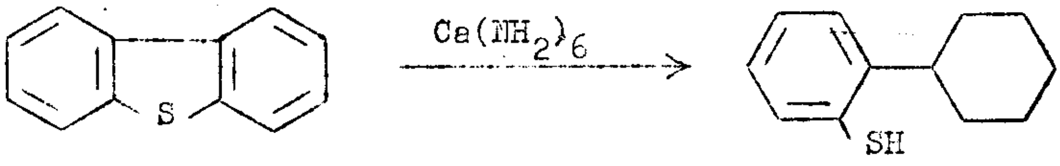
(IV)

When 1,4-dihydrodibenzothiophene is treated with phenyllithium under conditions identical with those employed in metelation a very smoth dehydrogenation occurs to yield dibenzothiophene, benzene, and lithium hydride.



(IV)

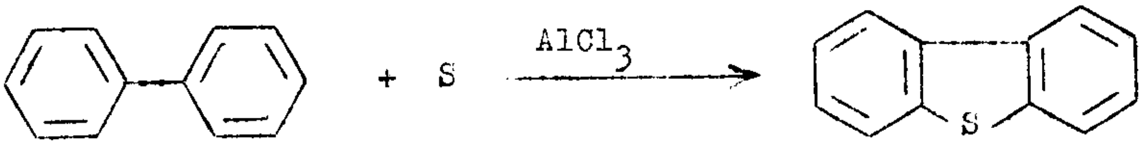
The electrochemical reduction of dibenzothiophene in ethylenediamine - lithium chloride solution has been shown to proceed via stepwise reduction of the aromatic nucleus followed by sulfur elimination (34, 35). Reduction of dibenzothiophene with calcium hexamine furnished o-cyclohexylthiophenol (V) as the major product in high yield (77 %).



(V)

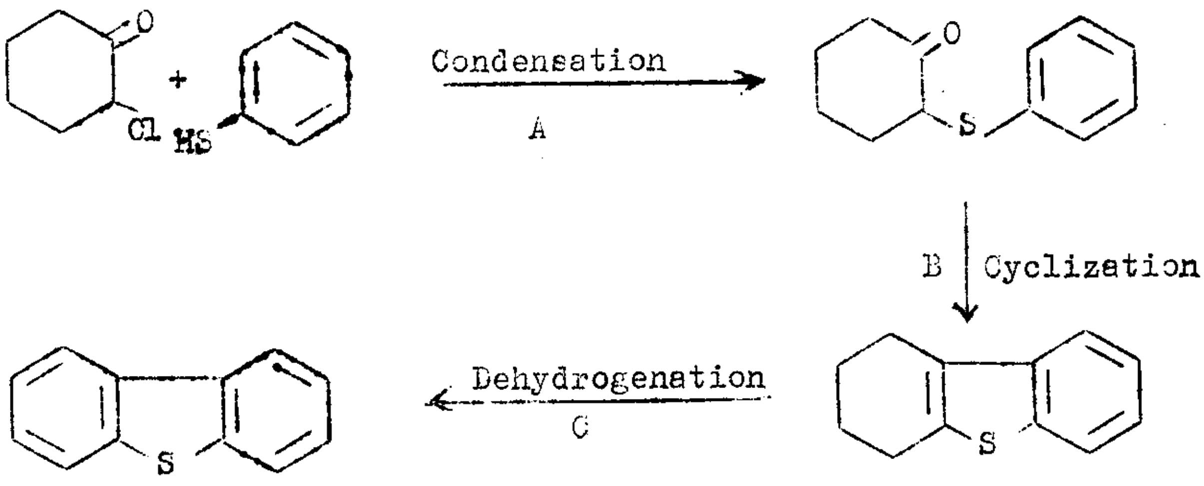
III) Synthesis of Dibenzothiophenes:

Dibenzothiophene was first synthesized by passing phenyl sulphide over heated iron nails (36). The best method for preparation of dibenzothiophene in high yields (up to 80 %) is by the action of sulfur on biphenyl in the presence of aluminium chloride (37).



A) Condensation of thiophenol with 2-chlorocyclohexanone

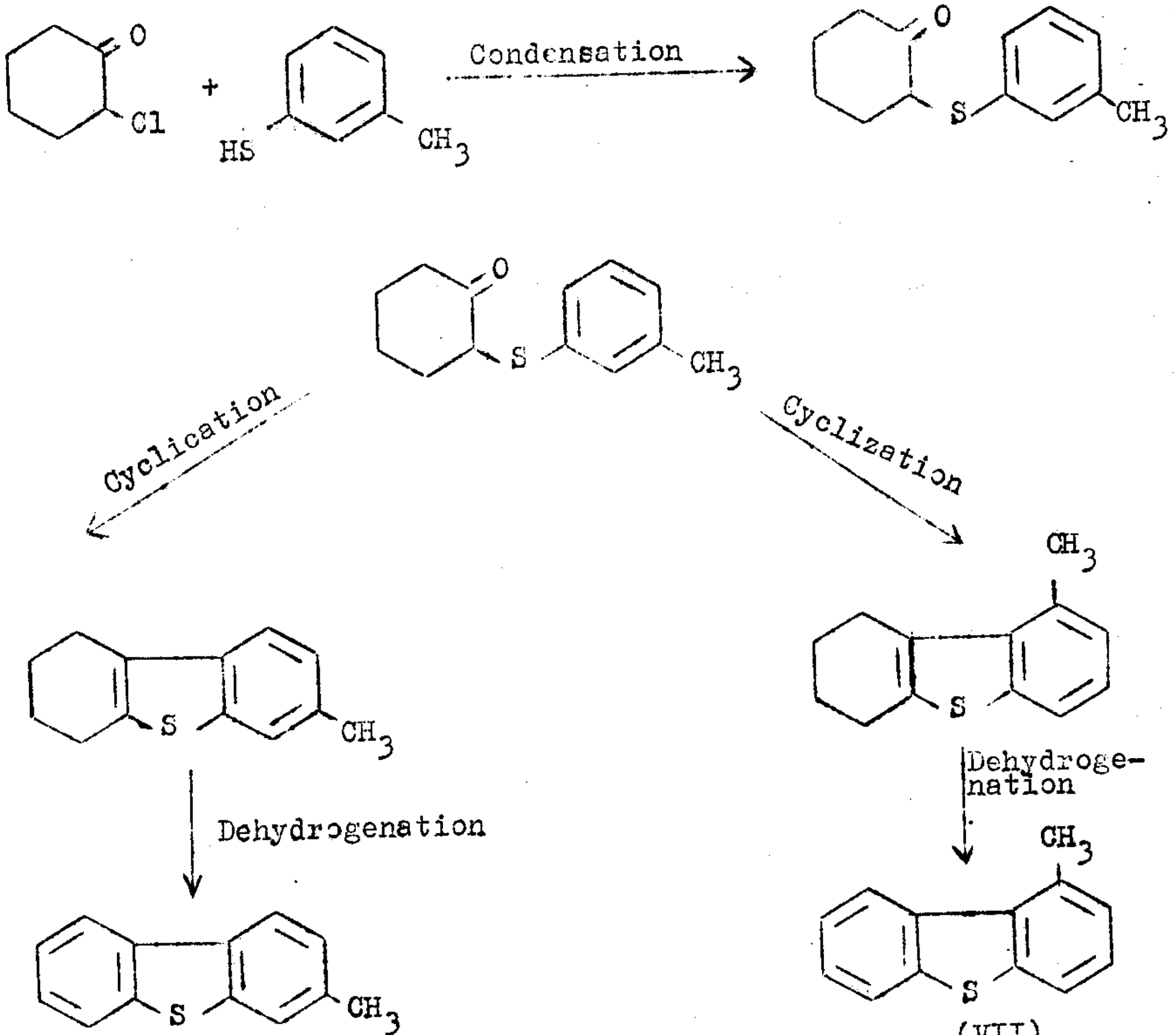
The most extensively studied new route to dibenzothiophenes, including dibenzothiophene, was devised simultaneously by Rabindran and Tilak (38) and McCall (39), which involve a condensation between thiophenol with 2-chlorocyclohexanone as illustrated in the following scheme:



Step A is best carried out using 2-chlorocyclohexanone, because it is more stable than the bromo analog. The use of aqueous sodium hydroxide as the condensing agent gave a low yields compared with similar examples where sodium ethoxide or potassium carbonate in acetone are used. Step B is usually conducted with phosphorous pentoxide at 180°C.

Dehydrogenation of the tetrahydrodibenzothiophene (Step C) was initially carried out using selenium metal at 300°C. A separate study of suitable reagents for step C has been made (40) in which it was observed that N-bromosuccinimide, although giving inferior yields, was effective at temperature as low as 75°C.

ortho-substituted thiophenols yield 4-substituted dibenzothiophenes, while para substitution results in the production of 2-substituted compounds. Conflicting reports occur on the use of meta-substituted thiophenols. Tilak (41) reports that m-thiocresol yields solely 3-methyl dibenzothiophene (VI), while McCall (39) reports a mixture of 1-methyl dibenzothiophene (VII) and 3-methyl dibenzothiophene (VI) which was separatable by column chromatography.



(VI)

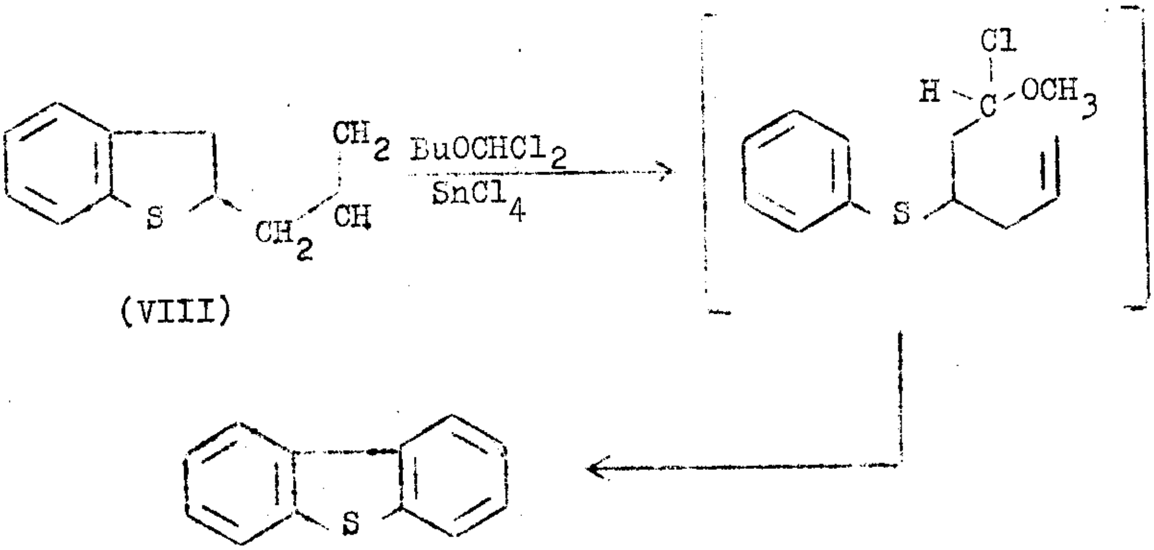
(VII)

p-Methoxythiophenol when condensed with 2-chlorocyclohexanone gave 2-methoxydibenzothiophene, but the synthesis of the later compound by this rout was abandoned due to a poor yield in step B (41). p-Nitrothiophenol condensed readily with the cyclohexanone but failed to cyclize with phosphorous pentoxide (41). In general terms, the reaction works well for thiophenols bearing electron-releasing substituents, but fails, or proceed in low yield, in the presence of electron-withdrawing groups. There are no recorded examples of substituted 2-chlorocyclohexanones being used.

B) From Benzo (b) thiophenes

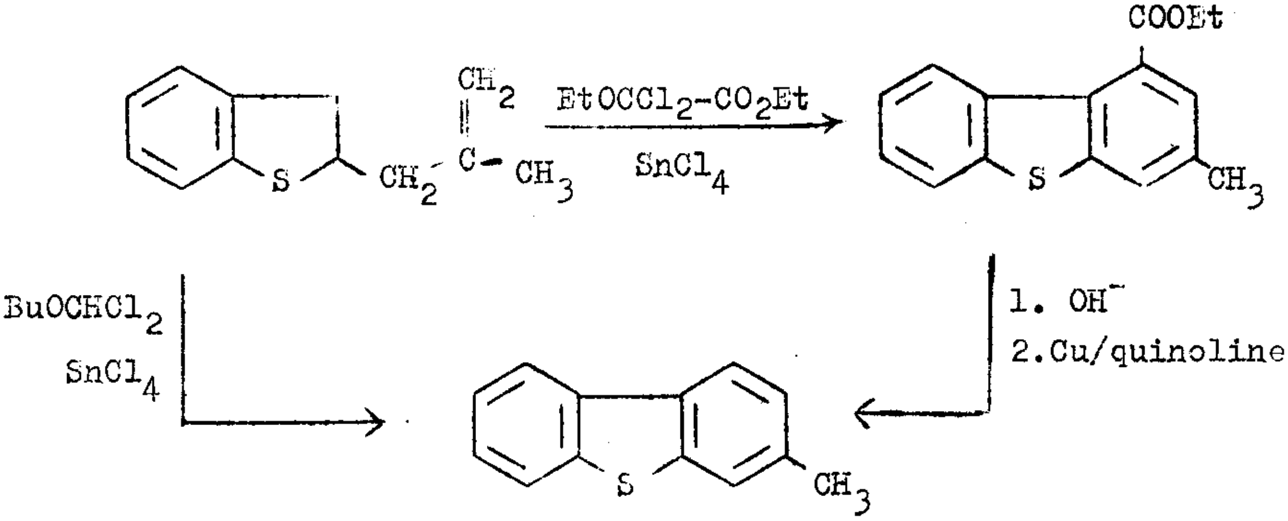
1) Reaction of dichloro ethers with allylbenzo [b] thiophenes

Dibenzothiphene has recently been synthesized from 2 allylbenzo(b) thiophene (VIII) by treatment with dichloromethyl butyl ether and anhydrous stannic chloride at low temperature as shown in the following equation (42):



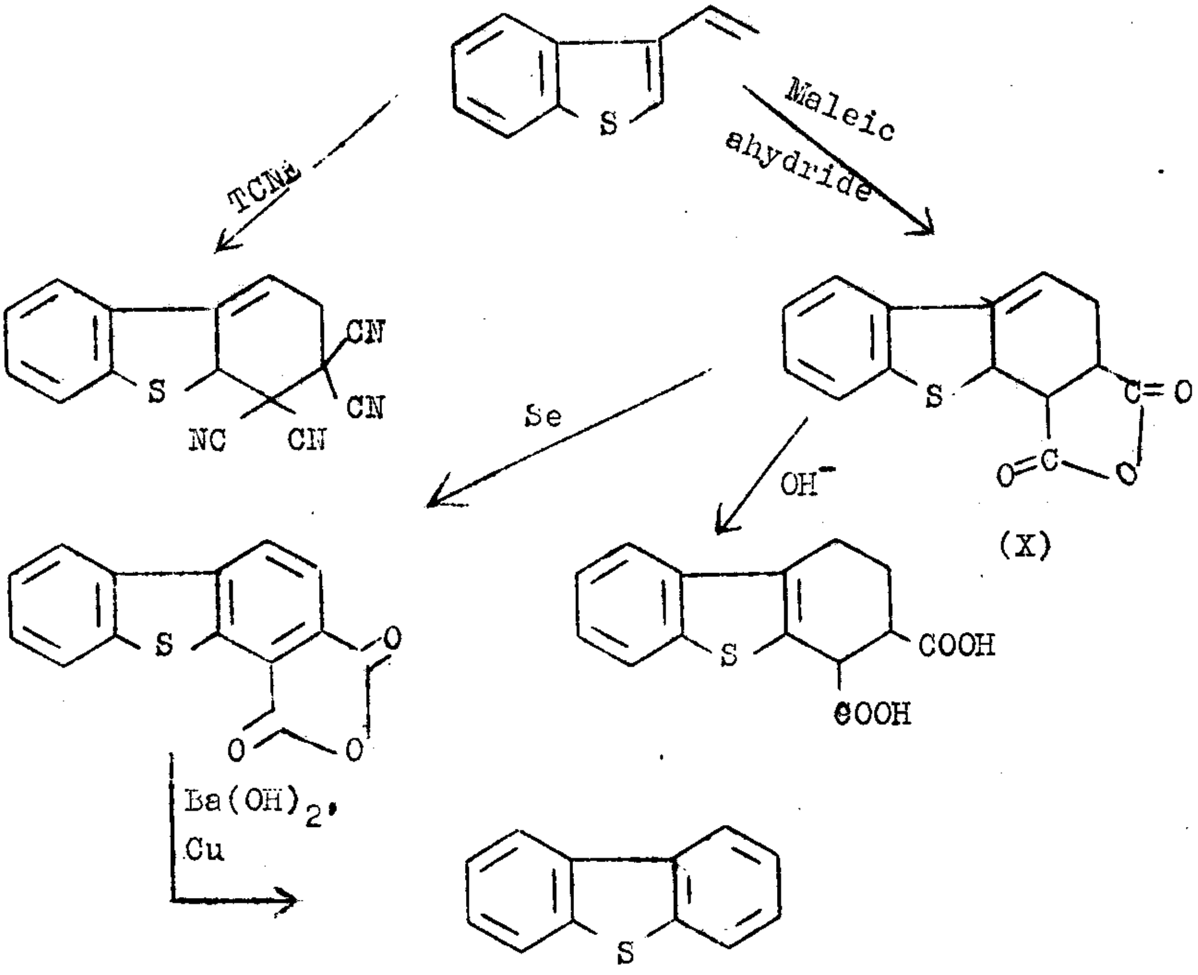
(VIII)

This sequence has been extended by the use of substituted allyl groups and modified formylating agent $EtOCCl_2$-COOEt, prepared from diethyl oxalate and phosphorous pentachloride (43), to yield dibenzothiophenes substituted in the 1-, 1, 3-, and 3-positions. The use of a substituted allyl group is shown in the following scheme:

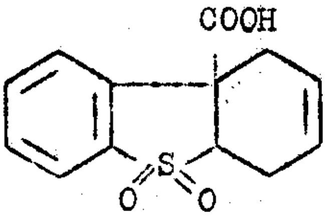


2) Diels-Alder Reactions

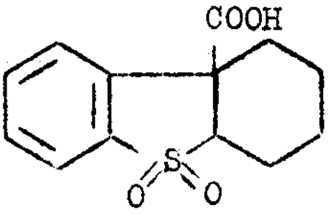
A novel route to produced dibenzothiphenes bearing substituents in the 3,4-positions involving treatment of 3-vinylbenzo(b)thiophene (IX) with maleic anhydride (44) or tetracyanoethylene (45) to give (X) and (XI) respectively as shown in the following scheme:



This type of Diels-Alder reaction has been extended to the synthesis of several other fused thiophene systems (44). The reaction of butadiene with the sulfone of 3-benzo (b)thiophene-carboxylic acid under Diels-Alder condition gives the adduct (XII). Catalytic reduction over platinum oxide removes the 2,3-double bond, yielding the compound (XIII) (46).



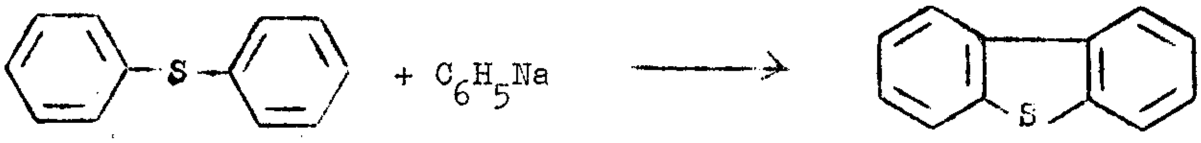
(XII)



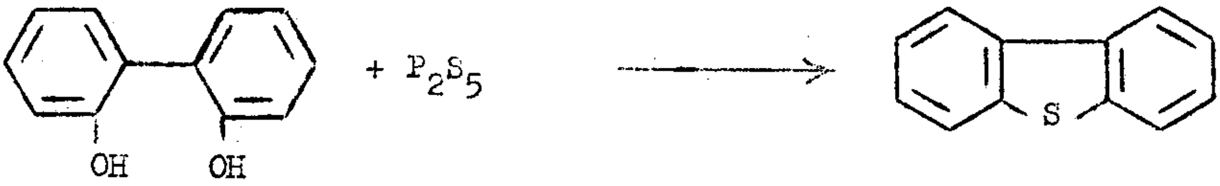
(XIII)

C) <u>Miscellaneous Methods</u>

Miscellaneous routes to dibenzothiophene include treatment of biphenyl sulfone with butyllithium to yield the 2,2'-dilithio derivative, which was cyclized with cuprous chloride to a mixture of dibenzothiophene and its sulfone (2:5) (47), and the action of phenylsodium (48) or potassium in dimethoxyethane (49) on biphenyl sulfide.



Dibenzothiophene was successively obtained from 2-hydroxybiphenyl (50) and 2,2'-dihydroxybiphenyl when treated with phosphorus pentasulfide.

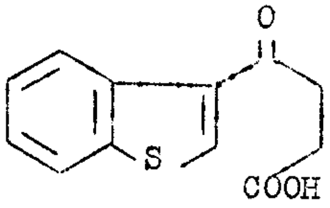


Armarego and Turner (51) has been described the Friedel-Crafts cyclization of biphenyl-2-sulfonyl chloride to give **dibenzothiophene** sulfone; however, thermal cyclization in octachloronaphthalene at 250°, under nitrogen, was reported to yield dibenzothiophene itself rather than the sulfone (52).

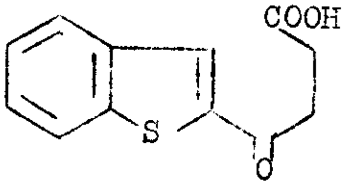
IV) Ring-Reduced Dibenzothiophenes

A) Ring ketones

Cagniant and Cagniant (53) have reported that succinoylation of benzothiophene under Friedel-Crafts conditions yields a separable mixture of the γ-ketobutyric acids (XIV) and (XV) in a ratio of 9:1 in a high combined yield (85 %). Huang-Minlon reduction of (XIV) to the butyric acid followed by cyclization of the derived acid chloride was reported to yield 4-keto-1,2,3,4-tetrahydrodibenzothiophene (XVI).



(XIV



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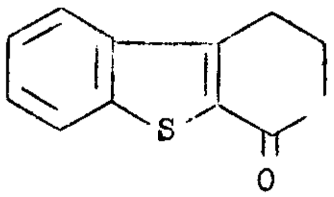
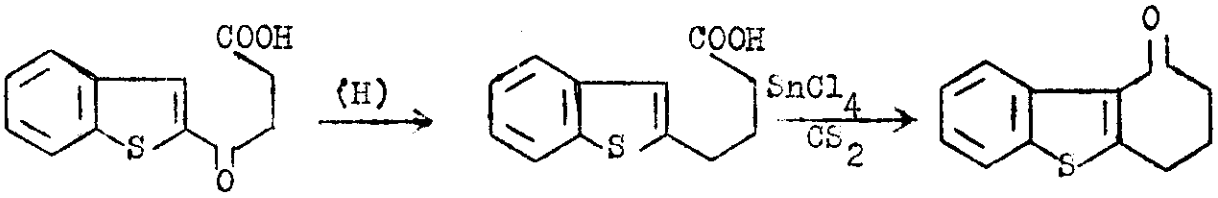


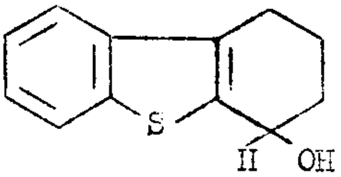
(XVI)

Alternatively, the keto acid (XIV) can be formed by reaction of the Grignard reagent from 3-bromobenzothiophene with succinic anhydride leading to (XVI) as described above (54). While Huang-Minlon reduction of (XV) to the butyric acid followed by cyclization with stannic chloride in carbon disulfide gave 1-keto-1,2,3,4-tetrahydrodibenzothiophene (XVII).

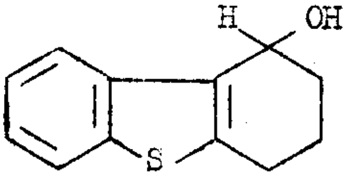


(XVII)

Reduction of the ketones (XVI) and (XVII) with sodium borohydride gave the secondary alcohols (XVIII) and (XIX), respectively, in high yield (55).

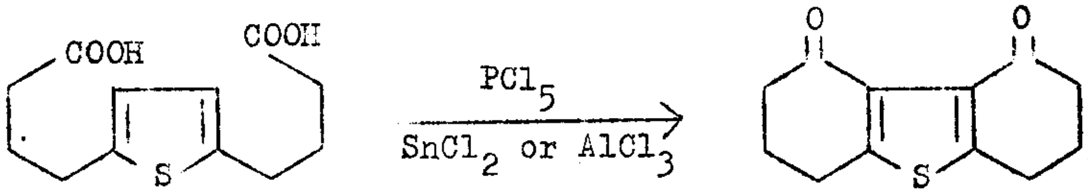


(XVIII)



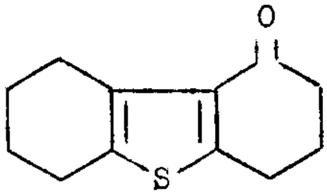
(XIX)

The total synthesis of dibenzothiophene from thiophene (56) has made available two ketones of potential synthetic interest. Stepwise succinoylation and reduction of thiophene cyclization of (XX) using phosphorus pentachloride in conjunction with anhydrous stannic chloride or aluminium chloride gave 1,9- diketo -1,2,3,4,6,7,8,9-octahydrodibenzothiophene (XXI).



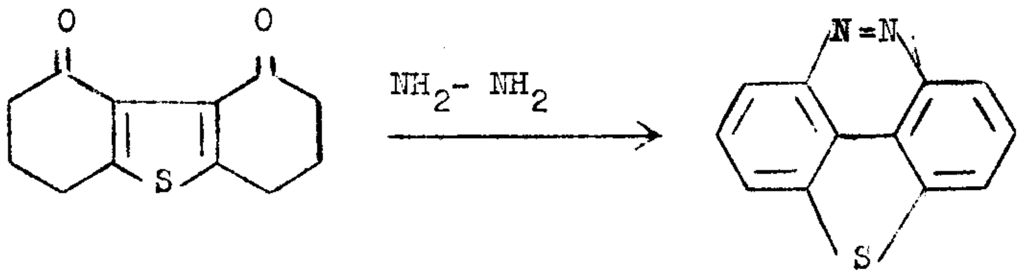
(XX) (XXI)

Alternatively, monocyclization of (XX) with phosphoric acid, followed by Huang-Minlon reduction and cyclization of the derived butyric acid yielded the ketone (XXII). Dibenzothiophene was obtained from both (XXI) and (XXII) via reduction and dehydrogenation.



(XXII)

The diketone (XXI) could be used to bridge the 1,9-positions of dibenzothiophene; for example, hydrazine could lead to (XXIII).

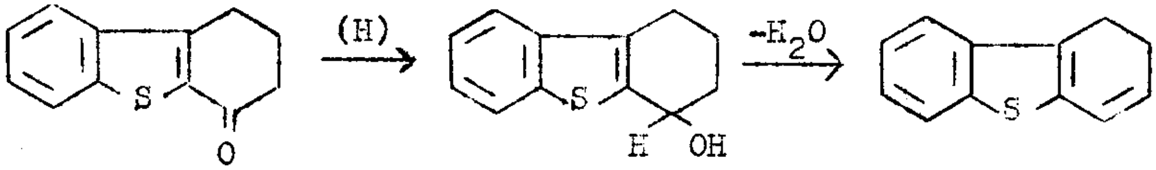


(XXIII)

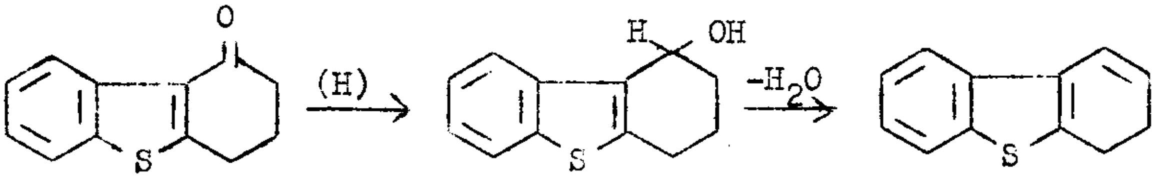
B) Hydrodibenzothiophenes

1) Dihydrodibenzathiophenes

Reduction of 4-keto-1,2,3,4- tetrahydrodibenzothiophene (XVI) with sodium borohydride followed by dehydration of the resultant carbinol (XVIII) by vacuum distillation in the presence of a trace of PPA yields 1,2-dihydrodibenzothiophene (XXIV) as a low-melting solid. Similarly, 3,4-dihydrodibenzothiophene (XXV) has been prepared from 1-keto compound (XVII) as an unstable liquid (55).



(XVI) (XVIII) (XXIV)

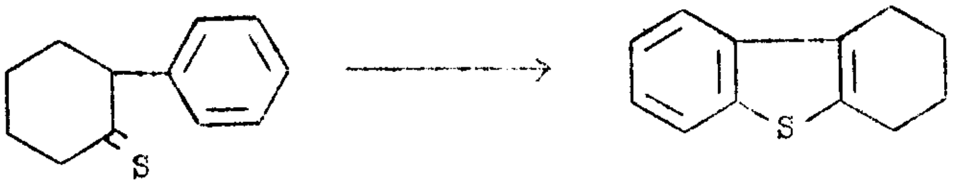


(XVII) (XIX) (XXV)

The reduction of dibenzothiophene with sodium in liquid ammonia to give a dihydro compound, probably 1,4-dihydrodibenzothiophene, has been discussed before.

2) Tetrahydrodibenzothiophenes

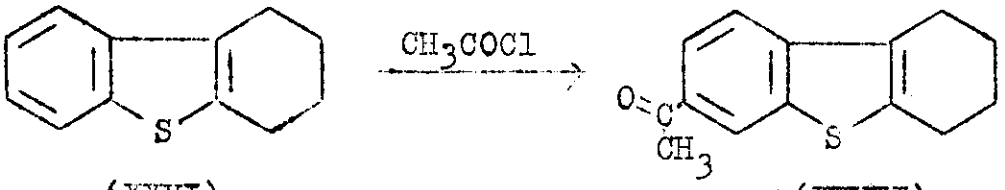
Cyclodehydration of 2-phenylthiocyclohexanone with a variety of reagents yielding 1,2,3,4-tetrahydrodibenzothiophene (XXVI) (39, 53, 57, 58), and represents the simplest way of obtaining this compound.



(XXVI)

Alternatively, reduction of 4-keto-1,2,3,4-tetrahydrodibenzothiophene (XVI) under Huang-Minlon conditions affords (XXVI) in high yield (53). Peracetic acid oxidizes (XXVI) to its sulfone (57, 59), which is readily reduced to (XXVI) again with LAH (57, 59).

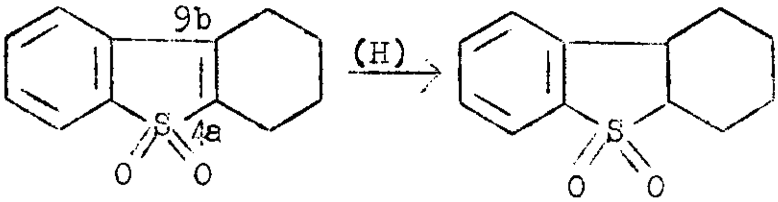
Friedel-Crafts acetylation of (XXVI) gives a monoacetyl derivative originally formulated as 8-acetyl-1,2,3,4-tetrahydrodibenzothiophene (53). Subsequent work (60, 61) revealed that it was in fact the 7-acetyl compound (XXVII).



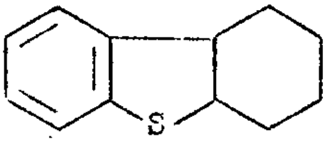
(XXVI) (XXVII)

3) Hexahydrodibenzothiophenes

The 4a, 9b double bond in 1,2,3,4-tetrahydrodibenzothiophene-5,5-dioxide (XXVIII) and similar compounds, is essentiallly nonaromatic and in this respect resembles the 2,3-bond in benzo (b) thiophene-1,1-dioxide (62). Catalytic reduction of (XXVIII) results in the formation of 1,2,3,4,4a, 9b-hexahydrodibenzothiophene-5,5-dioxide (XXIX). Subsequent reduction of (XXIX) with LAH yields 1,2,3,4,4a,9b-hexahydrodibenzothiophene (XXX) as an oil (63,64).



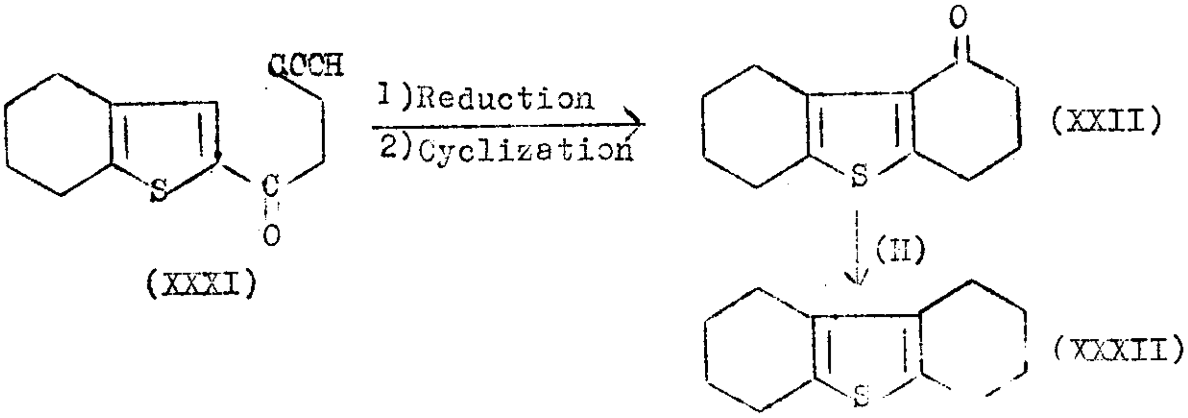
(XXVIII) (XXIX)



(XXX)

4) Octahydrodibenzothiophenes

1,2,3,4,6,7,8,9-Octahydrodibenzothiophene (XXXII) has been prepared by (53) Friedel-Crafts acylation of 4,5,6,7-tetrahydrobenzothiophene with succinic anhydride or with the ester chloride of succinic acid followed by hydrolysis, yields the keto acid (XXXI). Huang-Minlon reduction of the later compound followed by cyclization of the derived acid chloride with stannic chloride yields 1-keto- 1,2,3,4,6,7,8,9-octahydrodibenzothiophene (XXII) which on reduction gives (XXXII) in high yield.



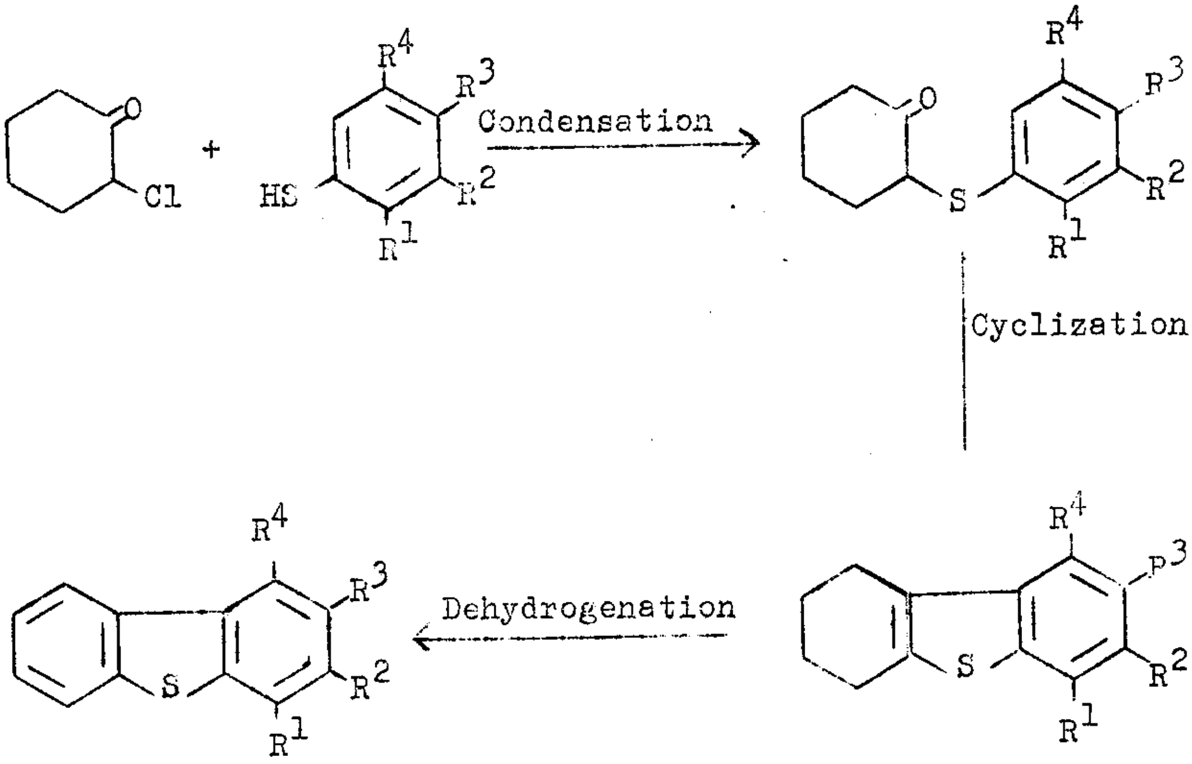
Alternatively, 1,2,3,4,6,7,8,9-octahydrodibenzothiophene (XXXII) has been prepared by reduction of the potassium salt of the enol tautomer of thiacyclohexanone with N-bromo-succinimide in benzene (65).

V) Derivatives of Dibenzothiophene:

A) Alkyl derivatives

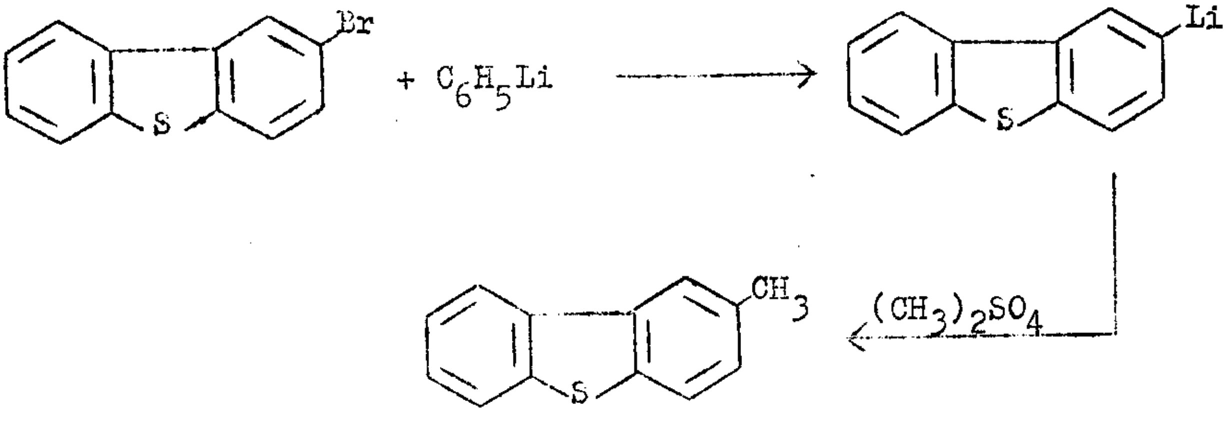
It is well known now, in the literature, a several ways for the syntheses of four monomethyldibenzothiophenes (41, 42, 66, 67) along with five dimethyl derivatives (3,11, 12, 51, 66, 67), two trimethyl derivatives (4), and eight tetramethyl compounds (4, 68, 69).

The mono methyl derivatives has been formed in good yield by the 2-chlorocyclohexanone route.



where R^1, R^2, R^3, R^4 = methyl group

Reductive silylation of 1-dibenzothiophene carboxylic acid yields the 1-methyl compound (42). 2-Methyl dibenzothiophene (XXXIII) is readily available from 2-bromodibenzothiophene via lithium exchange and treatment with dimethyl sulfate (66, 67).

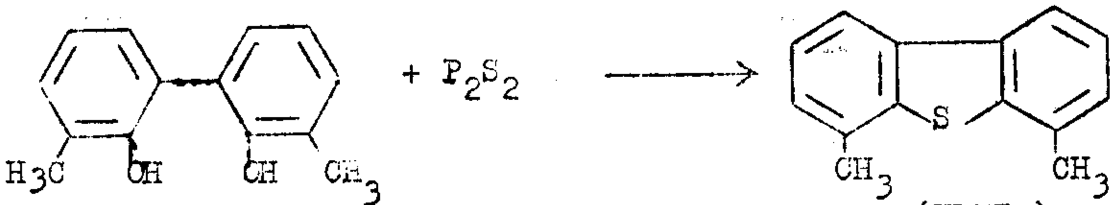


(XXXIII)

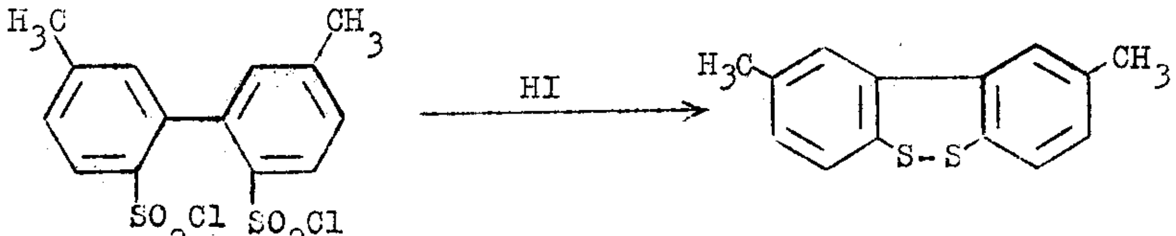
3-Methyldibenzothiophene is slightly less accessible than the other three isomers. It can be isolated by treatment of 3-lithiodibenzothiophene with dimethyl sulfate (67) or by Huang-Minlon reduction of 3-dibenzothiophene carboxaldehyde (66).

4-Methyldibenzothiophene is reported to be resistant to desulfurization with Raney nickel, which has been attributed to steric factors (3).

4,6-Dimethyldibenzothiophenen(XXXIV) has been isolated from several crude oils (3, 11, 12) and has been synthsized from 3,3'-dimethyl-2,2'-dihydroxydiphenyl with phosphorus pentasulfide (9).

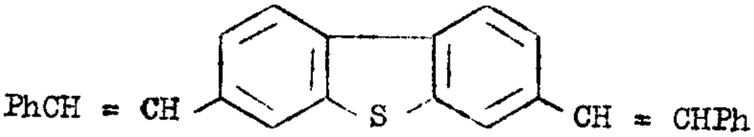

(XXXIV)

2,8-Dimethyldibenzothiophene is best prepared via lithium exchange with 2,8-dibromodibenzothiophene and treatment with dimethyl sulfate (67). It has also been formed via Huang-Minlon reduction of 2,8-dibenzothiophenedicarboxaldehyde (66). A novel route to the 2,8-dimethyl derivative has been described involving pyrolysis of 2,9-dimethyldibenzo-o-dithiin (XXXV), or its 5,5-dioxide, with copper bronze (51). The starting material is prepared by reduction of 5,5-dimethyl-diphenyl-2,2'-disulfonyl dichloride with hydrogen iodide in acetic acid.


(XXXV)

By the same route 3,7-dimethyldibenzothiophene has been rprepared (51) from the appropriately substituted disulfonyl dichloride.

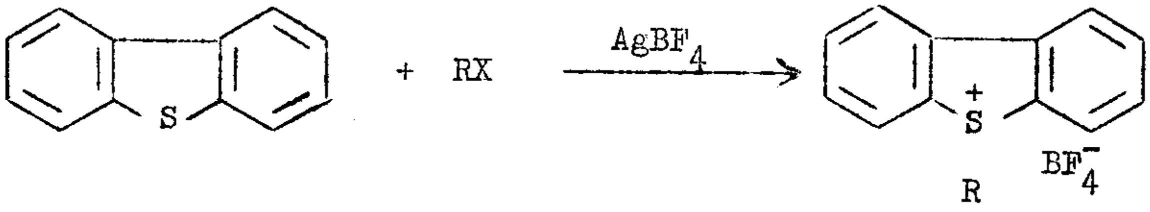
Both 2,8-dimethyl- and 3,7-dimethyldibenzothiophene have been reacted with a variety of aromatic aldehydes in DMF yielding distyryl compounds of type (XXXVI) (70).



(XXXVI)

B) S-Alkylthiophenium Salts

Treatment of dibenzothiophene with alkyl halides in the presence of silver tetrafluoroborate or triaryloxonium tetrafluoroborate has been shown to yield the corresponding 5-alkyl salts of type (XXXVII) (71,72). The products were thermally unstable, reverting to dibenzothiophene, although the corresponding perchlorates were more stable.

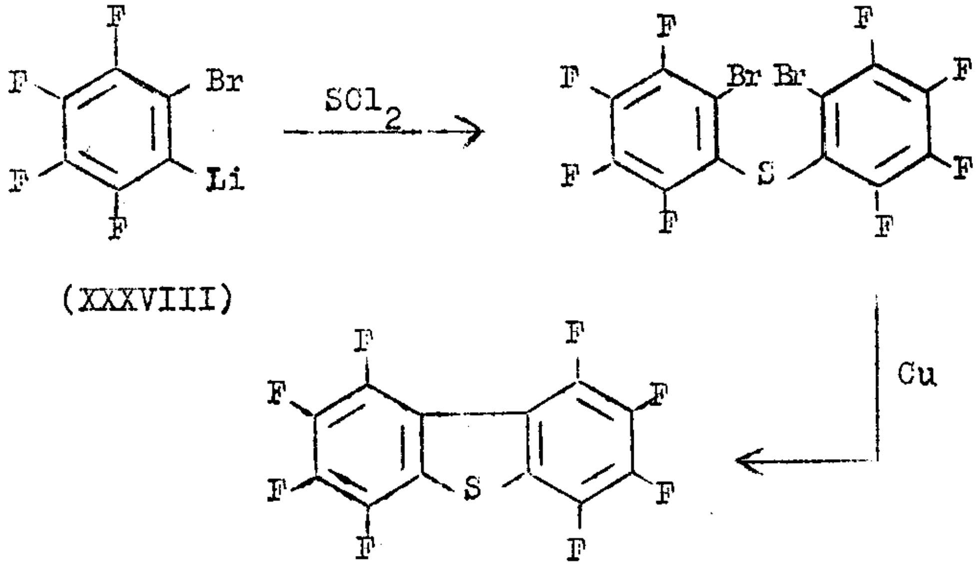


(XXXVII)

C) Halogen Derivatives

1. Fluorodibenzothiophenes

No monofluoro derivatives of dibenzothiophene have been reported. The reaction of 2-bromotetrafluorolithiobenzene (XXXVIII) with sulfur dichloride afforded bis(2-bromotetrafluorophenyl) sulfide which upon Ullman coupling gives octafluorodibenzothiophene (XXXIX) in quantitative yield (73).

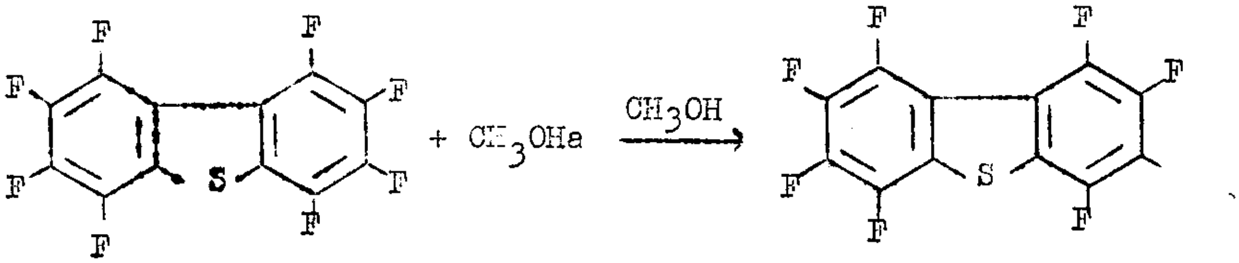


(XXXVIII)

(XXXIX)

The octafluoro compound (XXXIX) was smoothly desulfurized with Raney nickel to give 2,2'-dihydrooctafluorobiphenyl (74,75) and was recovered after heating for 4 days at 420°C in the presence of copper (76). Oxidation of octafluorodibenzothiophene (XXXIX) with the usual reagent proved difficult; however, 85 % hydrogen peroxide in trifluoroacetic anhydride smoothly converted it to the corresponding sulfone (74).

Reaction of octafluorodibenzothiophene (XXXIX) with sodium methoxide in methanol gave the 3-methoxy derivative (XL) together with a small amount of the corresponding 3,7-dimethoxy derivative (77).



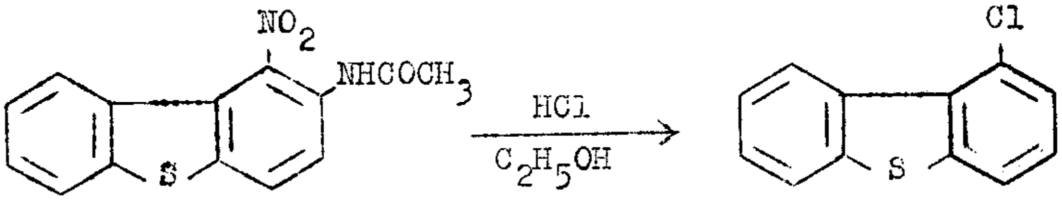
(XXXIX)

(XL)

2) <u>Chlorodibenzothiophenes</u>

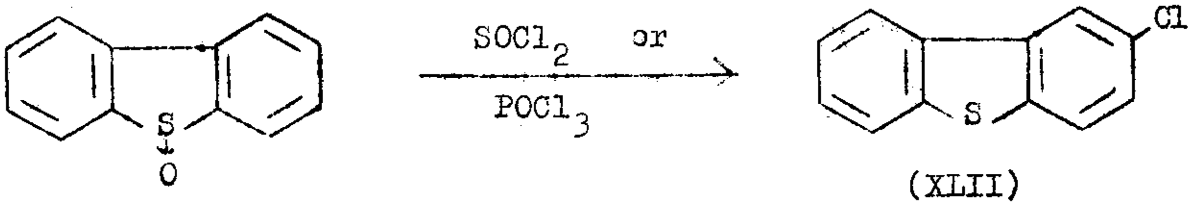
Chlorination of dibenzothiophene at low-temperature with elemental chlorine produces a chlorine adduct at the sulfur atom which is readily decomposed to dibenzothiophene-5-oxide. However, nuclear chlorination of dibenzothiophene has still not been studied. 2-Chlorodibenzothiophene has been prepared by the Sandmeyer reaction on 2-aminodibenzothiophene and this route has now been extended to give 1-chloro-, 3-chloro-, and 4-chlorodibenzothiophene (67).

An alternative route to 1-chlorodibenzothiophene involving treatment of 1-nitro-2-acetamidodibenzothiophene with ethanolic hydrogen chloride, in this case a nitrogen - free product was obtained and the product was shown to be 1-chlorodibenzothiophene (XLI) by comparison with an independently synthesized sample from 1-aminodibenzothiophene (67, 78).



(XLI)

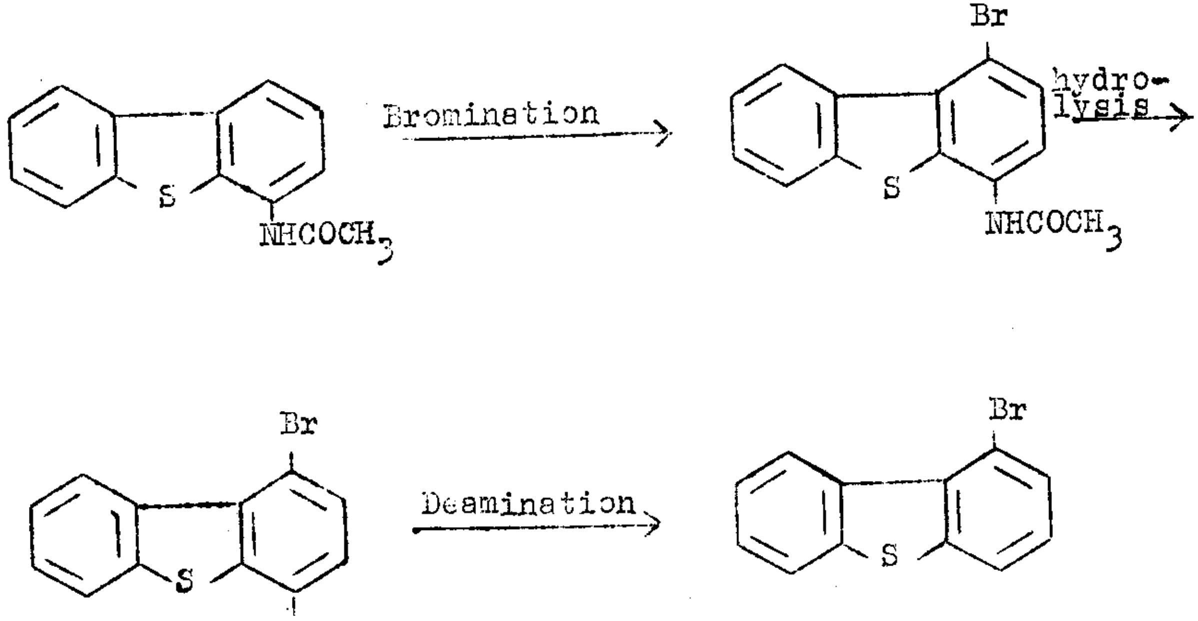
4-Chlorodibenzothiophene has been prepared in good yield via the o-chlorocyclohexanone route. Attempts to prepare the 2-chloro derivative by this route gave very low yields (39). Bird (79) show that dibenzothiophene-5-oxide did, in fact, react with either thionyl chloride or phosphorus oxychloride to yield 2-chlorodibenzothiophene (XLII) in good yield.



(XLII)

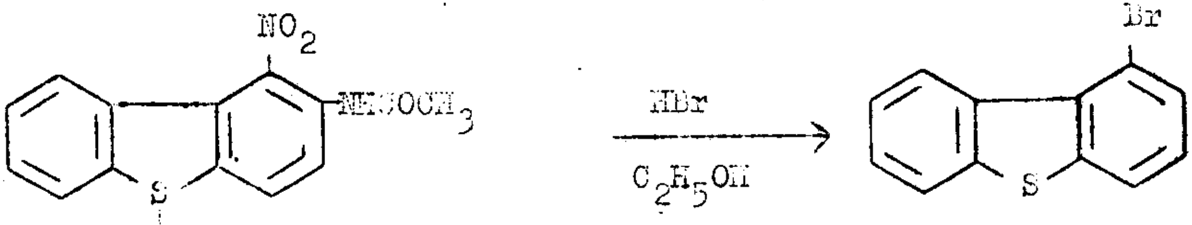
3) Bromodibenzothiophene

Two routes exist for the preparation of 1-bromodibenzothiophene (XLIII), each dependent on the ability of the acetamido group when present in position 2 or 4 of dibenzothiophene, to direct further substitution to the 1-position (80).



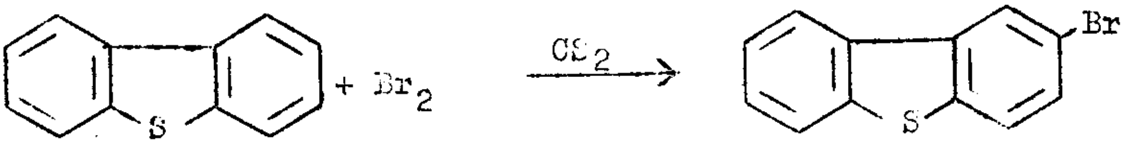
(XLIII)

Alternatively, 2-acetamidodibenzothiophene can be nitrated in the 1-position and the derived nitro amino converted to the 1-bromo derivative by treatment with hydrobromic acid in ethanol (78) akin to the reaction with ethanolic hydrogen chloride.



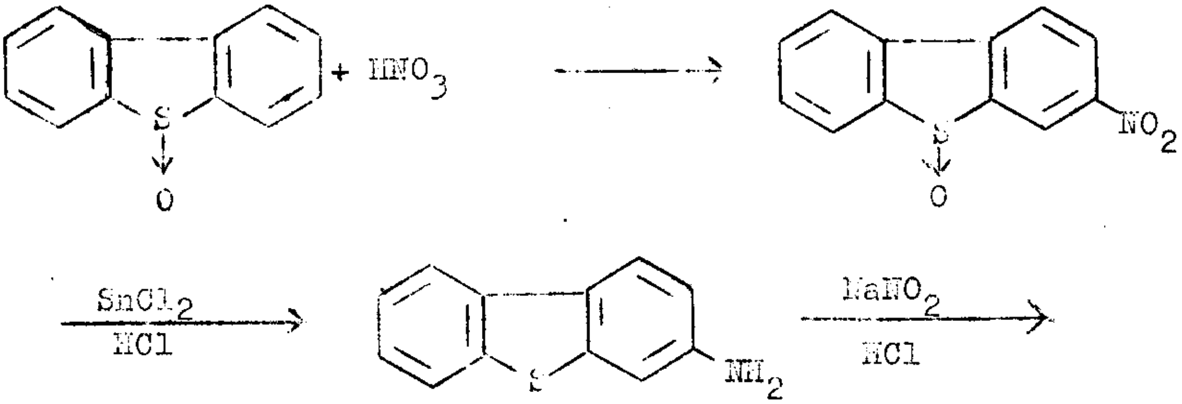
(XLIII)

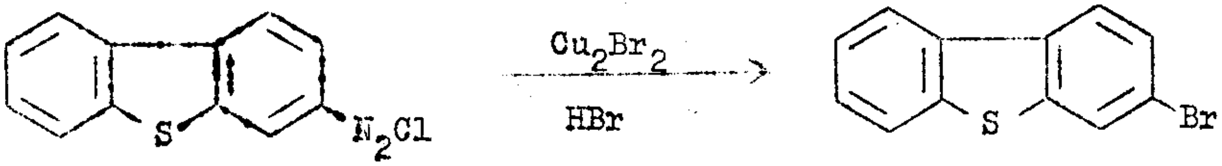
Bromination of dibenzothiophene in carbon disulfide readily affords the 2-bromodibenzothiophene (XLIV) (81).



(XLIV)

The usual route to 3-bromodibenzothiophene is via nitration of dibenzothiophene-5-oxide in the 3-position, followed by reduction with stannous chloride to 3-aminodibenzothiophene (82). The Sandmeyer reaction, on the later compound, with cuprous bromide in HBr yields the 3-bromodibenzothiophene (XLV) (83).





(XLV)

An alternative route to 3-bromodibenzothiophene could be employed involving nitration of dibenzothiophene-5,5-oxide in the 3-position followed by reduction of the nitro group and conversion to 3-bromodibenzothiophene-5,5-oxide via the Sandmeyer reaction (84). Reduction of the sulfone moiety with LAH (85) yields the 3-bromodibenzothiophene(XLV)

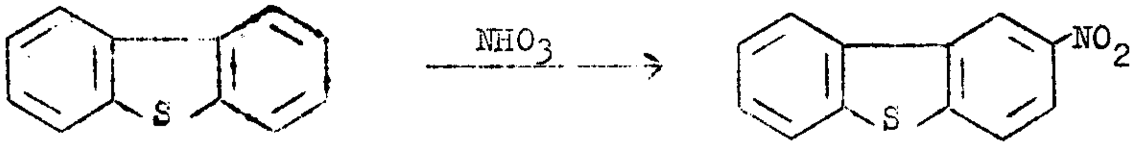
D) Hydroxy Derivatives

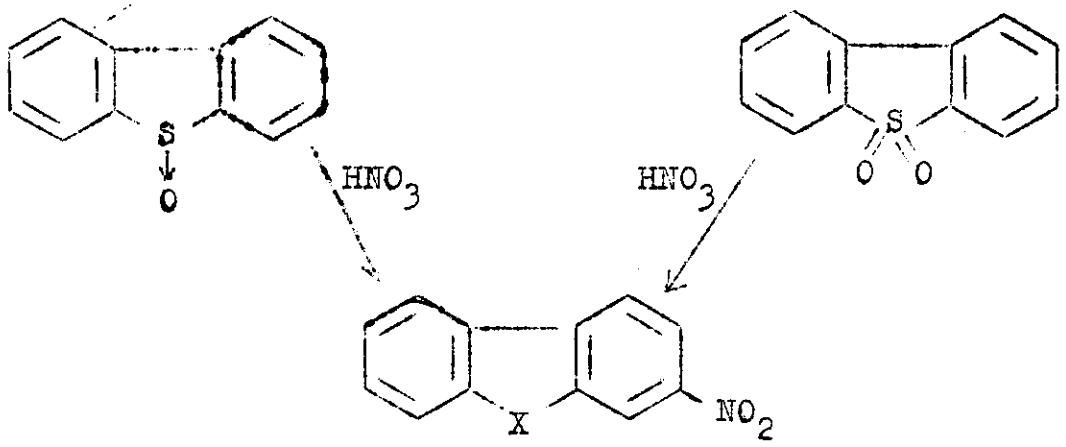
Hydroxydibenzothiophenes are obtained from the corresponding amino-, bromo- and lithio derivatives. Treatment of 2-bromodibenzothiophene with anhydrous potassium methoxide and copper bronze afforded 2-methoxy dibenzothiophene which on demethylation lead to 2-hydroxydibenzothiophene (86).

E) Nitrogen Derivatives

1) Nitrodibenzothiophenes

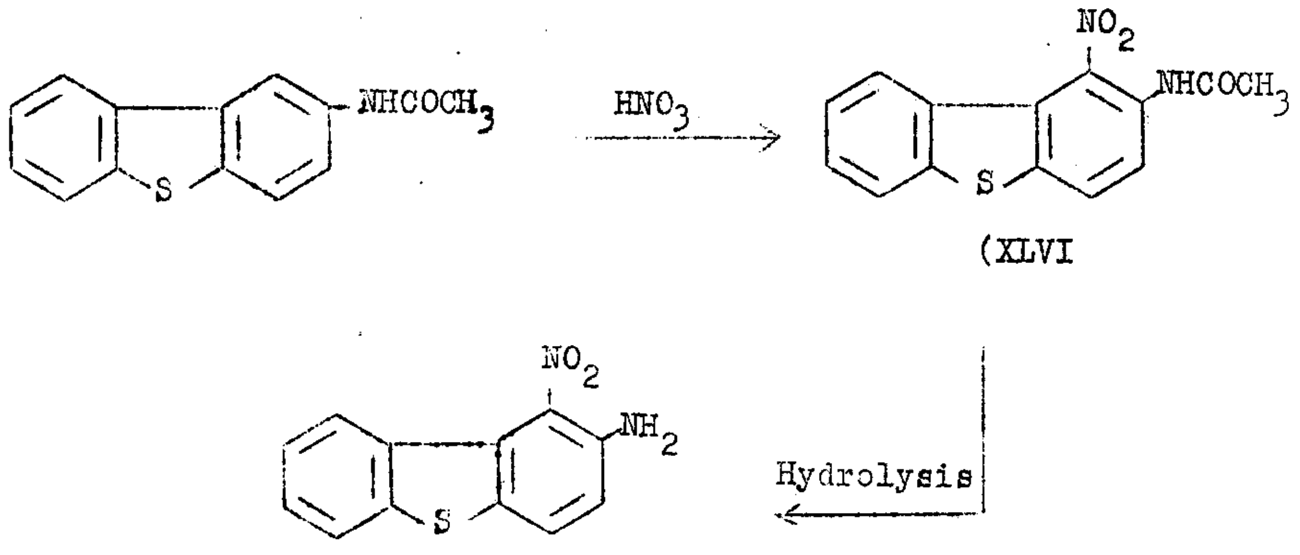
Direct nitration of dibenzothiophene occurs in the 2-position, while prior oxidation of the sulfur atom to either the sulfoxide or sulfone causes nitration to be directed to the 3-position.





X = SO or SO_2

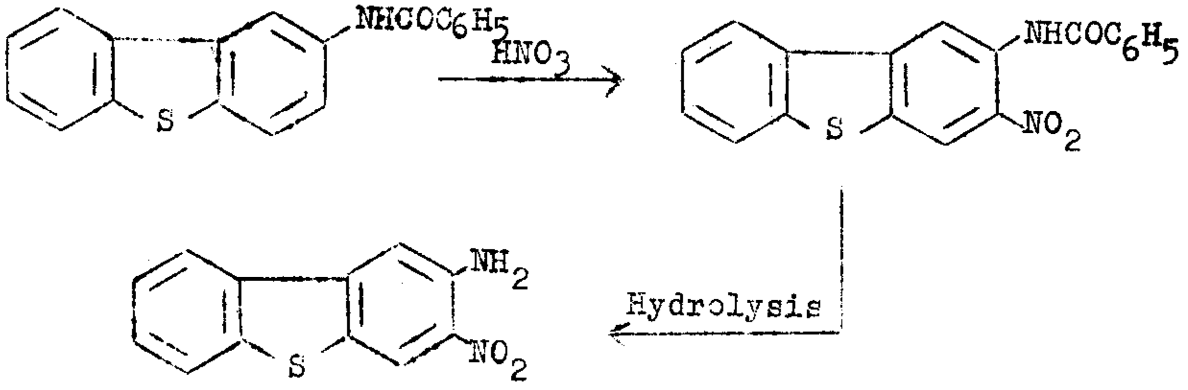
2-Acetamidodibenzothiophene is nitrated in the 1-position yielding 1-nitro-2-acetamidodibenzothiophene (XLVi), which upon hydrolysis with either sodium hydroxide or ethanolic hydroiodic acid gives 1-nitro-2-aminodibenzothiophene (XLVII) (78). The same nitroamine (XLVII) was also formed by the nitration and hydrolysis of 2-carbethoxyaminodibenzothiophene (87).



(XLVII)

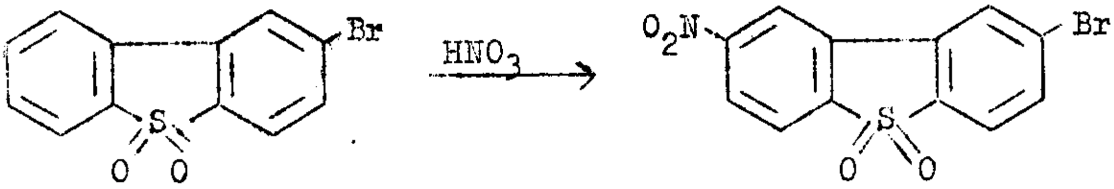
Deamination of (XLVII) via diazotization in sulfuric acid afforded 1-nitrodibenzothiophene (78).

In contrast to the behavior of the 2-acetamidodibenzothiophene, nitration of 2-benzenesulfonamidodibenzothiophene (87) and 2-benzamidodibenzothiophene (88) results in the production, after hydrolysis, of 2-amino-3-nitrodibenzothiophene (XLVIII).



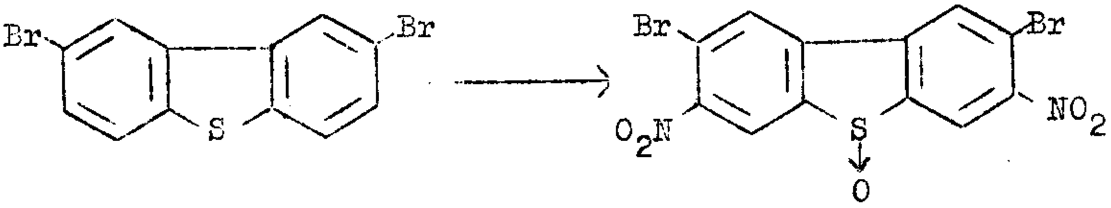
(XLVIII)

Nitration of 2-bromodibenzothiophene-5,5-oxide gave 8-nitro-2-bromodibenzothiophene (XLIX) (85).



(XLIX)

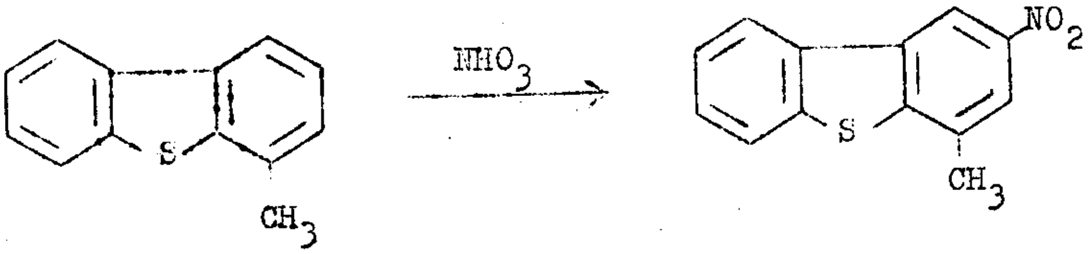
Nitration of 2,8-dibromodibenzothiophene gave a product which was assigned structure (L), while attempts to nitrate 2,8-dibromodibenzothiophene-5,5-dioxide were unsuccessful (89).

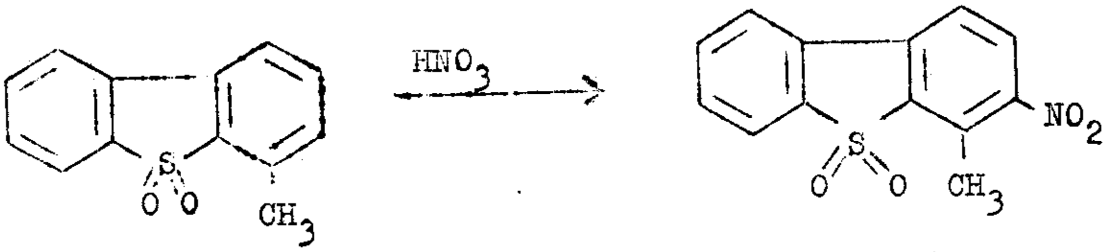


(L)

As mentioned earlier, oxidation of dibenzothiophene to either the sulfoxide or sulfone causes electrophilic attack to occur at the 3-position rather than at the normal 2-position. This trend is further exemplified by the behavior of 4-methyldibenzothiophene which is nitrated in the 2-position, while nitration of 4-methyldibenzaothiophene which is nitrated in the 2-position, while nitration of

4-methyldibenzothiophene-5,5-dioxide occurs in the 3-position yielding (LI) (90).





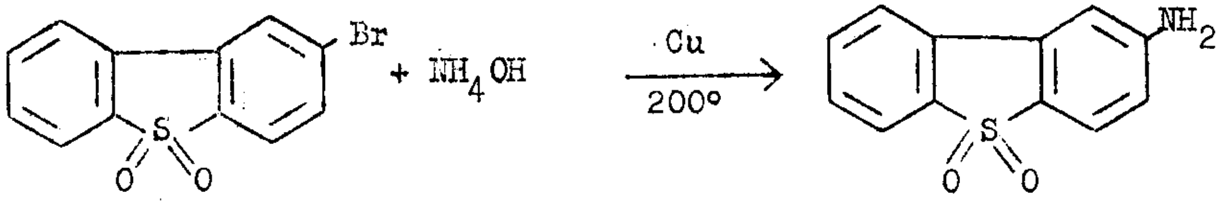
(LI)

2. Aminodibenzothiophenes

1. Aminodibenzothiophene (LII) can be prepared by reduction of the corresponding nitro compound with hydrogen and Raney nickel (78).

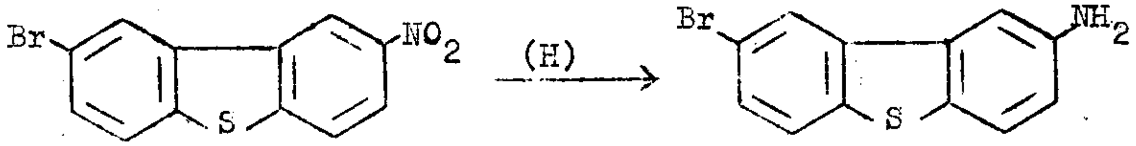
(LII)

A synthesis of 2-aminodibenzothiophene-5,5-oxide (LIII) from the corresponding 2-bromo compound has been described involving heating with ammonium hydroxide and copper at 200°C (91).

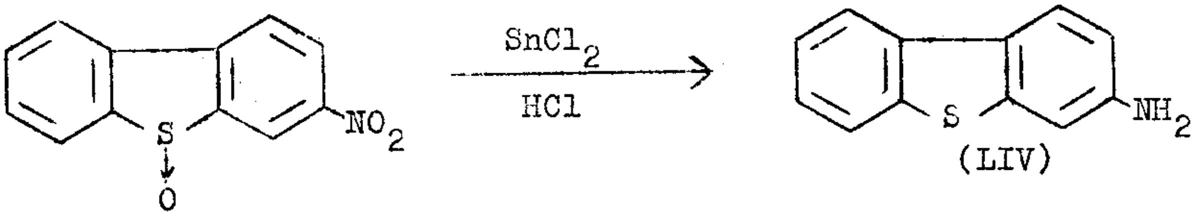


(LIII)

8-Bromo-2-aminodibenzothiophene has been prepared by catalytic reduction of the corresponding nitro derivative (85).



3-Aminodibenzothiophene (LIV) is prepared by reduction of 3-nitrodibenzothiophene-5-oxide with stannous chloride at room temperature (82, 92).



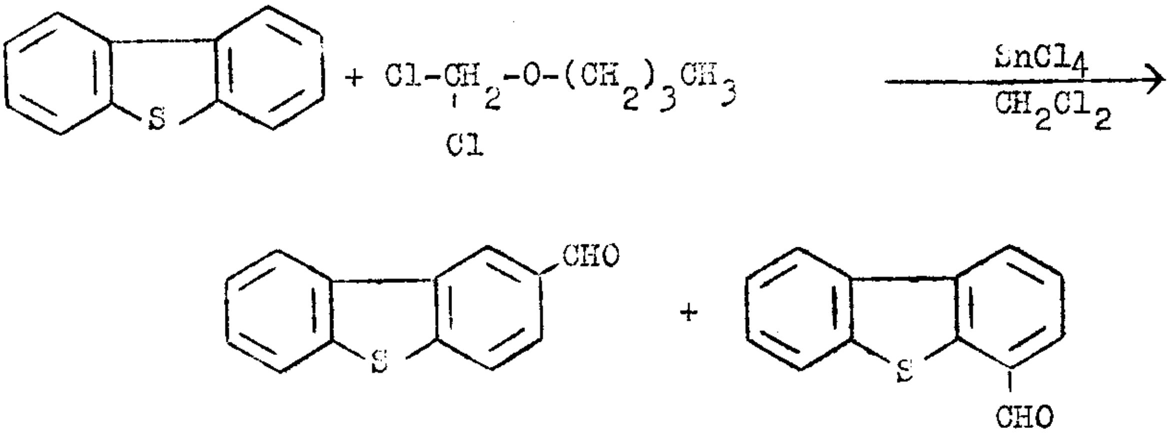
(LIV)

F) Side-Chain Carbonyls

1) Aldehydes

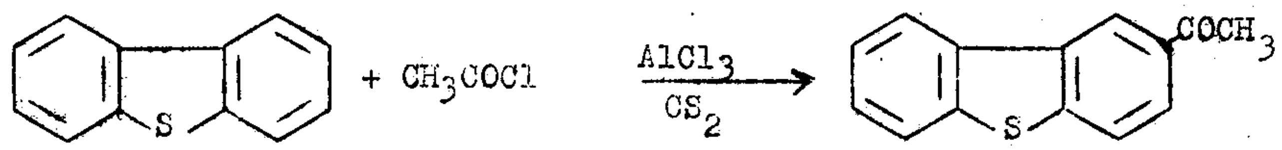
Two approaches to the synthesis of the aldehydes of dibenzothiophene have been made. The most successful method involves treatment of the appropriate bromodibenzothiophene with butyllithium and dimethylformamide (66, 90, 93, 94).

The formylating reagent α,α-dichloromethyl butyl ether (95) has been employed (96, 97) for the formylation of dibenzothiophenes. Using this reagent on dibenzothiophene in methylene chloride, with stannic chloride as catalyst, Elmes and Swan obtained a mixture of the 2- and 4-aldehydes (97). Purification by fractional crystallization gave 4-dibenzothiophenecarboxaldehyde.



2) Ketones

2-Acetydibenzothiophene (LV) was isolated by Gilman (84) by treatment of dibenzothiophene in carbon disulfide with acetyl chloride and aluminum chloride.

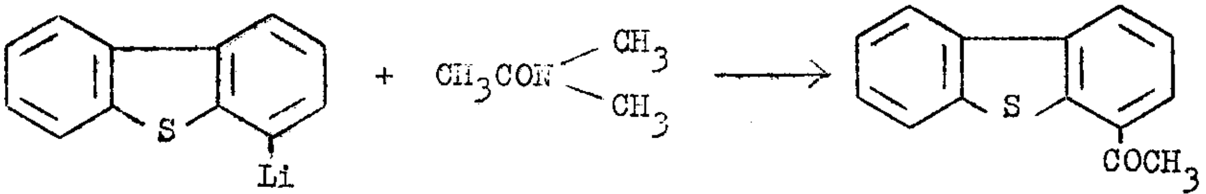


(LV)

Andreeva and Koton (98, 99) have reported that conducting the acetylation in benzene or toluene yields an inseparable mixture of 2- and 3-acetyldibenzothiophene, while use of either carbon disulfide or nitrobenzene yields a similar mixture from which 2-acetyl compound was isolated by solvent extraction.

The kinetics of the Friedel-Crafts acetylation of dibenzothiophene in nitroethane have been studied; the reaction proceeds approximately five times faster than with toluene as substrate (100, 101).

The most convenient method of preparation of acetyldibenzothiophenes is via treatment of the appropriate lithio derivative with N,N-dimethylacetamide. In this way 2-acetyl and 4-acetyldibenzothiophene (LVI) have been prepared (66).



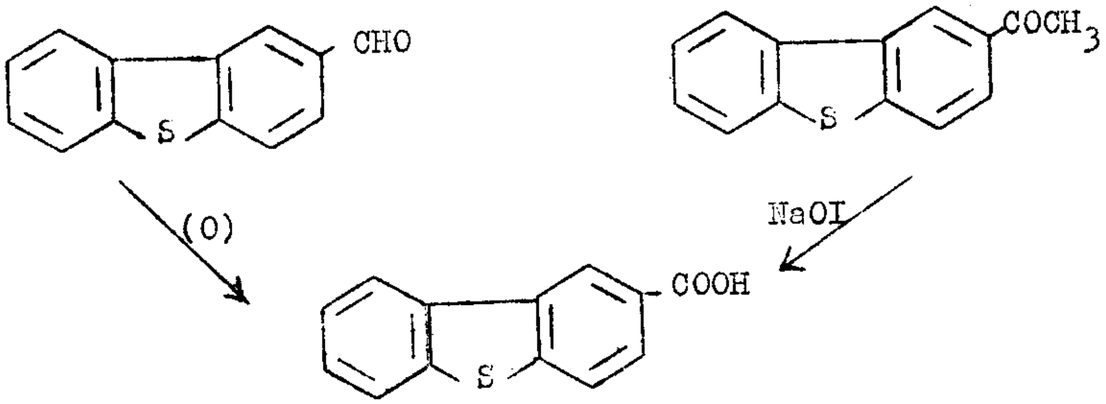
(LVI)

Oxidation of 2-acetyldibenzothiophene with peracetic acid yields the corresponding sulfone and with sodium hypoiodite, 2-dibenzothiophene carboxylic acid (102).

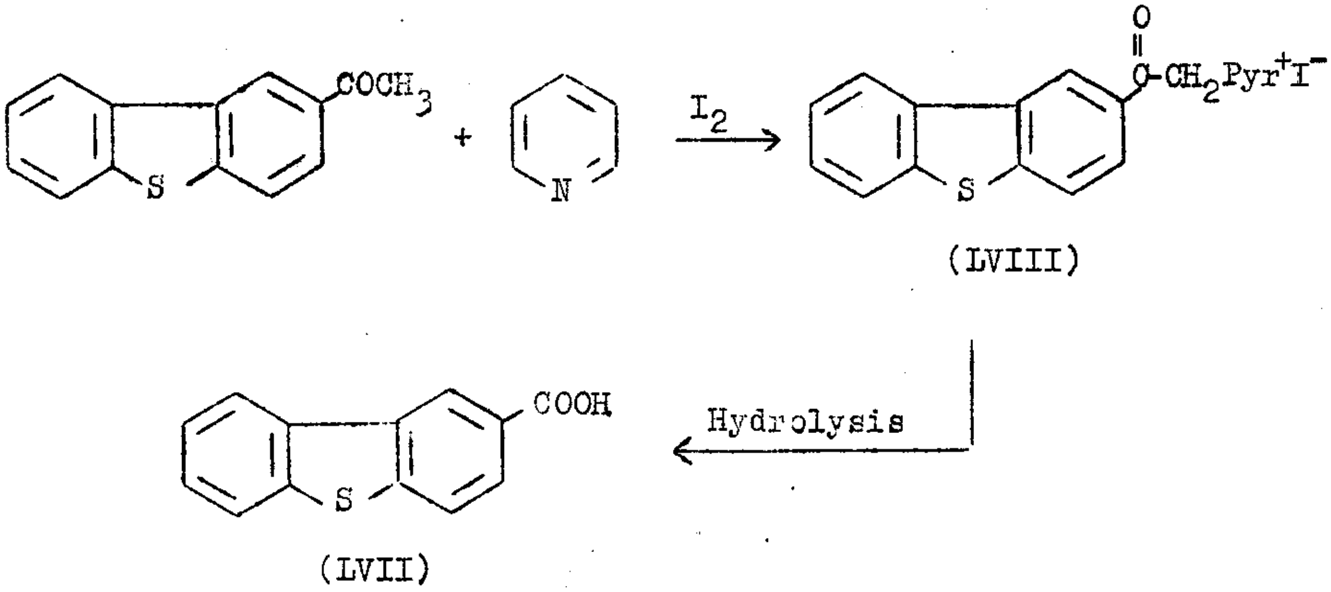
G) Acids

1) Nuclear Carboxylic Acids

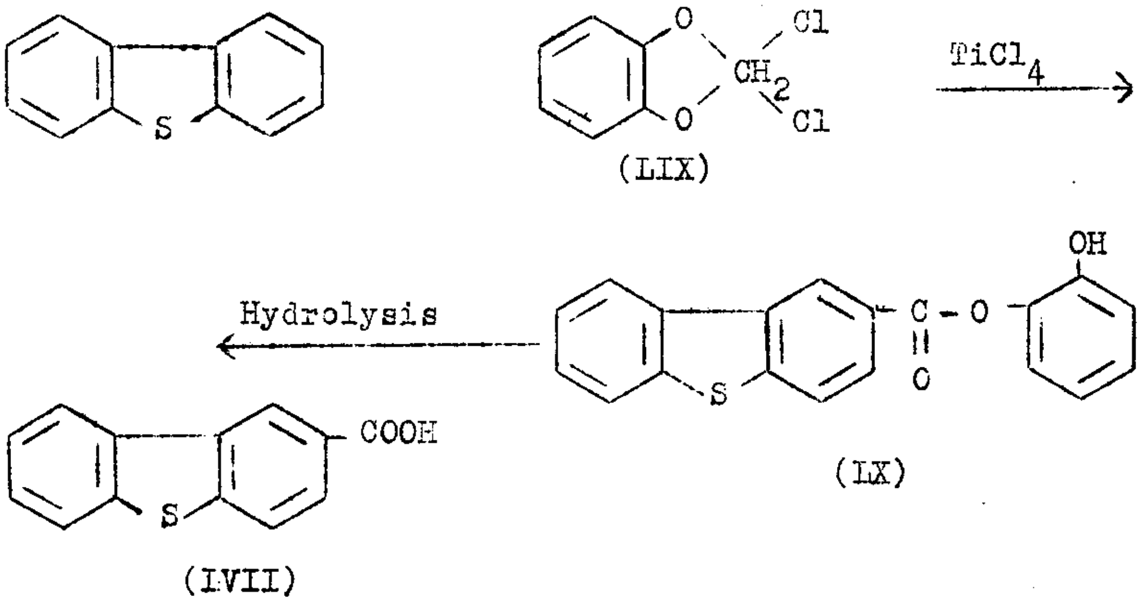
2-Dibenzothiophenecarboxylic acid (LVII) has been prepared by oxidation of the corresponding aldehyde (97, 102) or by sodium hypoiodide oxidation of the corresponding acetyl derivative (102).



Reaction of 2-acetyldibenzothiophene with anhydrous pyridine and iodine yields the acetyl pyridinium salt (LVIII), hydrolysis of which yields the 2-acid (LVII). The same sequence has been carried out on 2-acetyldibenzothiophene-5,5-dioxide (102).



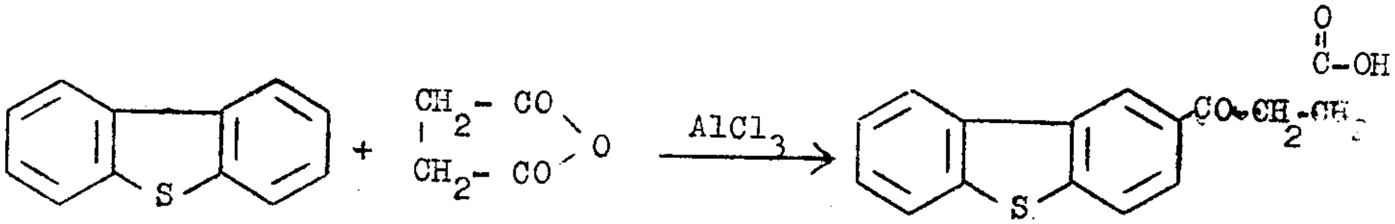
Reaction of pyrocatechol dichloromethylene acetal (LIX) with dibenzothiophene in the presence of titanium tetrachloride yields O- hydroxyphenyl-2-dibenzothiophenecarboxylate (LX) (102). The complete obsence of the 4-isomer in this reaction may be due to steric effects at the 4-position between the sulfur atom and the bulky reagent. Hydrolysis of (LX) yields 2-dibenzothiophenecarboxylic acid (LVII)(102).



The most efficient method of preparing the 2-acid is via carbonation of 2-lithiodibenzothiophene (66). 4-Methyl-3-dibenzothiophenecarboxylic acid has been prepared by carbonation of the corresponding lithio derivative (90).

2) -oxo-dibenzothiophenebutyric Acids

Friedel-Crafts acylation of dibenzothiophene with succinic anhydride is known to occure in the 2-position, yielding γ-oxo-2-dibenzothiophenebutyric acid (LXI).



(LXI)

A separate study has been made of the acylation and diacylation of dibenzothiophene with succinic anhydride or the ester chloride of succinic acid (103). The use of either reagent gave good yields of (LXI) and in each cases the use of excess reagent gave 2,8-disubstitution, although the best yield of 2,8-disubstitution was obtained by using the succinic ester followed by hydrolysis.

A low yield of γ-oxo-4-dibenzothiophenebutyric acid has been obtained by treatment of 4-lithiodibenzothiophene with succinic anhydride (104).

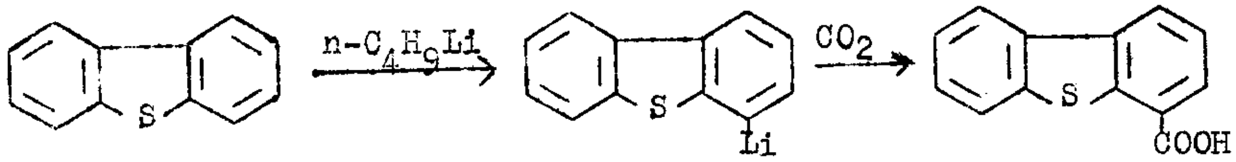
3) Sulfonic Acids

Many highly substituted derivatives of dibenzothiophene bearing sulfonic acid groups are described in the patent literature relating to optical brighteners and dyestuffs; however, the structures of these compounds are very rarely established (105-107).

The 3,7-disulfonyl chloride of dibenzothiophene-5,5-dioxode has been isolated from the reaction of biphenyl with chlorosulfonic acid. The reaction proceeds via the 2,4,4-trisulfonyl chloride of biphenyl (108).

H) Lithio and Other Metallic Derivatives

The formation of 4-lithiodibenzothiophene from dibenzothiophene and butyllithium has been investigated by several groups of workers (90, 104, 109, 110-113) including the optimum conditions for the formation of this compound (114). In this study the direct lithiation of dibenzothiophene was accomplished with methyl, n-butyl, and phenyllithium in various solvents and at varied temperatures, each reaction being quenched with carbon dioxide and the yield of 4-dibenzothiophenecarboxylic acid being taken as a measure of the overall efficiency of the reaction. From this work, it is clear that mixed tetrahydrofuran-diethyl ether is the solvent of choice and 0° the optimum reaction temperature.



The formation of 1-lithio- (67, 109, 112), 2-lithio-(66, 67, 109, 112, 113) and 3-lithiodibenzothiophene (66, 67, 109, 112) has been achieved by translithiation of the appropriate bromodibenzothiophene with butyllithium, Higher yields of derivatives are obtained from 2-lithiodibenzothiophene by conducting the reactions at 0° (66) rather than at room temperature (67). Both 2-lithio- and 3-lithio-4-methyldibenzothiophene have been prepared from the respective bromo derivative (90), and a similar synthesis of 1-lithio-4-methoxydibenzothiophene has been described (93).

Both 2,8-dilithio- (66, 67, 115) and 3,7-dilithiodibenzothiophene (115) have been obtained from the corresponding dibromides and in the former case it has been demonstrated that higher yields of derived product are obtained at 0°(115) rater than at room temperature (67). Attempts to directly dilithiate dibenzothiophene with an excess of butyllithium have been largely unsuccessful. Termination of the reaction with carbon dioxide gave the 4-acid as sole product (116).

Metallation of dibenzothiophene-5-oxide with three equivalents of butyllithium followed by carbonation gave a mixture of 4-dibenzothiophene carboxylic acid (36 %) and dibenzothiophene (10 %) (117).

Phenylcalcium iodide metallates dibenzothiophene in the 3-position; however, it has no effect on the corresponding sulfone (118). Mercuration of dibenzothiophene has been accomplished by adding mercuric acetate to a melt of dibenzothiophene, but the position of mercuration was not established. Mercuric nitrate or bisulfite give no identifiable products (118).

Dibenzothiophene-5-oxide reacts with triaryltin chlorides to give complexes which show bacteriostatic and fungistatic properties (119).

III- DISCUSSION