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CHEMISTRY OF BENZO[b]THIOPHENE-2,3-DIONE

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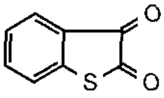
Abstract–The synthesis and reactions of benzo[b]thiophene-2,3-diones are presented in this review. References to miscellaneous studies on the title compound are also included.

INTRODUCTION

In connection with a current project being carried out in our laboratory, we found it necessary to review the literature regarding the synthesis and reactions of benzo[b]thiophene-2,3-dione (**1**). The synthesis and chemistry of **1** has been discussed as a subtopic in reviews on benzothiophenes.[2] In 1939 Candea[2] published a review on the development of benzo[b]thiophene-2,3-diones with reference to their chemistry, constitution and properties. Hartough and Meisel have reviewed[2] the synthesis and chemistry of benzo[b]thiophene-2,3-diones up to 1953. Iddon and Scrowston have discussed[2] some aspects of the chemistry of benzo[b]thiophene-2,3-diones. We have made an attempt to compile the literature concerning with the synthesis, reactions, and physical properties of benzo[b]thiophene-2,3-diones. It is anticipated that this would provide the reader with an overall picture of the trend in the interest in benzo[b]thiophene-2,3-diones. The related indole-2,3-dione (isatin) was the subject of comprehensive reviews by Sumpter[3] and by Popp.[3]

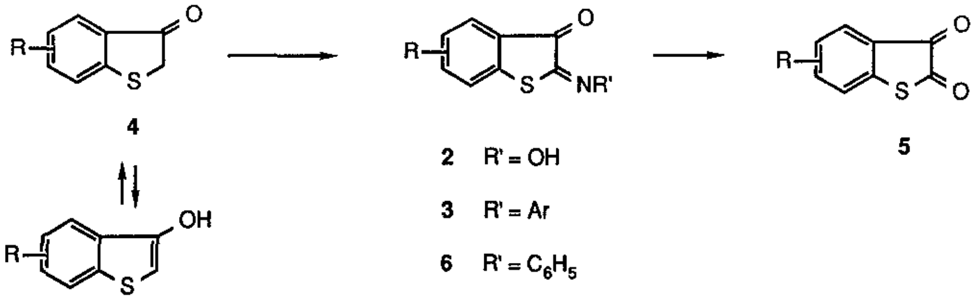


1

It should be noted that **1** has been, in the past, referred to by several names viz. thionaphthenequinone, 2,3-thianaphthenedione, 2,3-thianaphthenequinone, 2,3-diketodihydrothionaphthene, benzo[b]thiophene-2,3-quinone, thioisatin, and benzo[b]thiophene-2,3-dione; the latter being the current nomenclature.

SYNTHESIS OF BENZO[b]THIOPHENE-2,3-DIONES

The most frequently used method for the preparation of benzo[b]thiophene-2,3-diones is via the acid hydrolysis of the 2-oximes (**2**) or 2-anils (**3**) of benzo[b]thiophene-2,3-diones. The oximes (**2**) are usually prepared by the treatment of thioindoxyl (**4**) with nitrous acid.[4] Hydrolysis of the oximes (**2**, R = H or 5-methyl) using hydrochloric acid gave **1**[4,5,6] and 5-methylbenzo[b]thiophene-2,3-dione (**5**, R = 5-methyl).[7]



4

4

2 R' = OH

3 R' = Ar

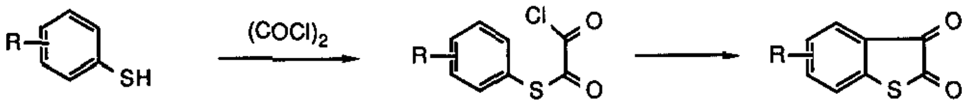
6 R' = C_6H_5

7 R' = p-Me_2N-C_6H_4

5

The 2-anils of benzo[b]thiophene-2,3-dione (**3**) are also prepared from thioindoxyl. Thus, thioindoxyl (**4**, R = H) has been converted to anil **6** by bromination, and subsequent reaction of the 2,2-dibromobenzo[b]thiophene-3-one with aniline.[8-11] Hydrolysis of **6** using hydrochloric acid furnished **1**.[8-11] Another method of preparing **6** is by treatment of **4** (R = H) with nitrosobenzene.[5,12] Similarly, reaction of thioindoxyl with p-nitrosodimethyl aniline gave **7**, which was converted to **1** by allowing it to react with dilute mineral acids.[5,11,13-15] Utilizing this approach, appropriately substituted **7** has been converted to 5-bromo,[16,17] 6-bromo,[18] 4-chloro,[19] 5-chloro,[5,16,20] 6-chloro,[18,21] *7-chloro,*[5,19] *5-fluoro,*[16] *6-fluoro,*[18] *5-iodo,*[16] *6-*iodo,[18] 5-nitro,[22] 6-nitro,[22] 5-ethyl,[15] 6-ethoxy,[8,23,24] 4-methyl,[19] 5-methyl,[5,17,19,25,26] 7-methyl,[19] 5-methoxy,[27] 6-methoxy,[28,29] benzo[b]thiophene-2,3-diones (**5**). This synthetic scheme (vide supra) has been effective in the synthesis of 5,6-dimethoxy,[27] 5-chloro-7-methyl,[8,23] 6-chloro-4-methyl,[8,21,23,24] and 5-chloro-6-methyl[30] and other disubstituted benzo[b]thiophene-2,3-diones (**5**).[31-34] The synthesis of thioindoxyls (**4**) from various starting materials has been reviewed by Hartough and Meisel (ref. 2, pp 68).

Treatment of thiophenols (**8**) with oxalyl chloride followed by cyclization of the intermediate **9** is a convenient method for the synthesis of benzo[b]thiophene-2,3-diones. Usually a Lewis acid, such as aluminum chloride,



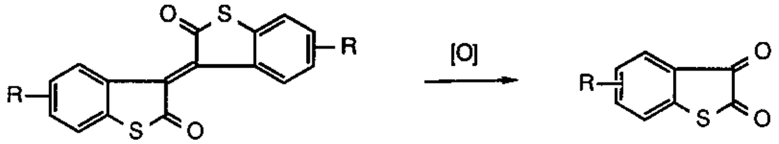
8

9

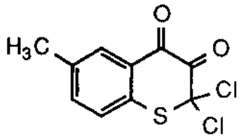
5

is used to effect ring closure of the acid chloride. This method is currently most prevalent for the synthesis of **1** from thiophenol.[16,20,35-38] Appropriately substituted thiophenols have been used for the preparation of benzo[b]thiophene-2,3-diones such as 5-methyl[17,37,39] and 5-ethylbenzo[b]thiophene-2,3-dione.[17] In the synthesis of **5** (R = 4,6-dimethoxy) from 3,5-dimethoxythiophenol the use of Lewis acid is not necessary to effect the cyclization of **9** (R = 3,5-dimethoxy).[40] This approach, however, is not applicable to the synthesis of 5-halobenzo[b]thiophene-2,3-diones. The presence of halogen deactivates the phenyl ring in **9** (R = 4-Cl)[20] sufficiently to prevent cyclization.

Benzo[b]thiophene-2,3-diones (**5**) have also been obtained from the oxidation of thioindigo. Ozonolysis of thioindigo (**10**, R = H) gave **1** as the product.[41] 6-Ethoxy and 6-chloro-4-methylbenzo[b]thiophene-2,3-diones were obtained in low yields on ozonolysis of the parent thioindigo.[41] 6-Chloro and 6-chloro-4-methylbenzo[b]thiophene-2,3-diones, and **1** have been synthesized by treatment of the appropriate thioindigo (**10**, R = 6-chloro, R = 6-chloro-4-methyl, R = H) with aqueous potassium hydroxide followed by acidification.[21] Nitrosation of **10** (R = H) in acetic acid resulted in the formation of **1**.[42]



10 **5**



11

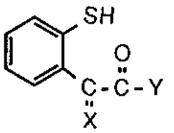
When heated in water, compound **11** has been reported[43] to undergo hydrolytic ring opening and subsequent recyclization to give 5-methylbenzo[b]thiophene-2,3-dione. The mechanism for this ring contraction has been discussed.[43]

REACTIONS OF BENZO[b]THIOPHENE-2,3-DIONES

As seen with isatins,[3] reactions of benzo[b]thiophene-2,3-diones can be broadly classified into two categories: Reactions that involve ring opening of the heterocycle and reactions involving the carbonyls without cleavage of the C-S bond.

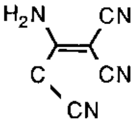
A. Ring opening reactions.

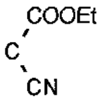
On treatment with alkali, **1** undergoes cleavage of the C-S bond to form 2-mercaptophenylglyoxalic acid (**12a**). Reaction of **12a** with chloroacetic acid in the presence of base gives benzo[b]thiophene-2,3-dicarboxylic acid (**13**).[8-11,44] 5-Methyl, 5-ethyl, and 6-methoxy analogs of **13** have been prepared from the corresponding 5-substituted benzo[b]thiophene-2,3-diones.[17,29,39] In an analogous fashion **1** reacts with chloroacetone in the presence of alkali to give **14**.[8] With chloroacetaldehyde the product of the ring opening and subsequent cyclization reaction is **15**.[45] The reaction of **5** (R = 5-ethyl) with phenacyl bromide in the presence of alkali gave the 2-benzoyl analog **16**;[17] and under similar conditions reaction of **1** with 4-ethylphenacyl bromide furnished **17**.[17] Compound **18** was obtained from the reaction of benzo[b]thiophene-2,3-dione (two equivalents) with 1,3-dichloropropanone,[9] whereas, 6-chloro-4-methylbenzo[b]thiophene-2,3-dione when allowed to react with 1,3-dichloropropanone in acetic anhydride yielded **19**.[46,47] The ketone **20** was synthesized from the reaction of **1** with **21**.[46,47]

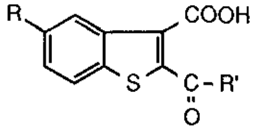


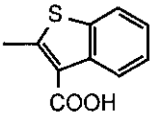
12a X = O, Y = OH

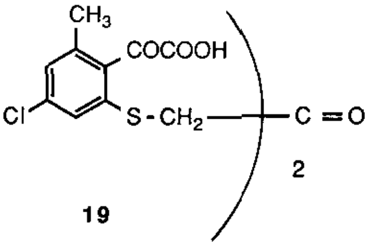
12b X = NH, Y = NH_2

12c X =  , Y = OH

12d X =  , Y = OH



	R	R'
13	H	OH
14	H	Me
15	H	H
16	Et	Ph
17	H	p-Et-C_6H_4
18	H	



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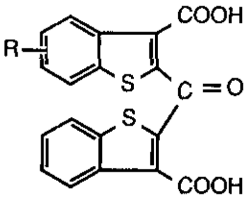

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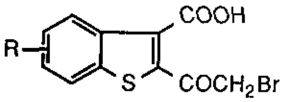
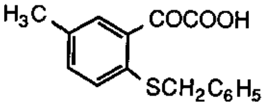


21

In the presence of alkali, **1** (and **5**, R = 5-methyl) have been reported to undergo ring opening to give the corresponding sodium salts of **12a**. Addition of benzyl chloride to the reaction yielded **22**, whereas treatment with Raney alloy gave **23**.[37] Reaction of **5** (R = H; 5-methoxy; 6-methoxy; 5,6-dimethoxy) with α-chlorophenyl acetic acid results in the formation of **24**.[27,28] Compound **12a** has also been obtained from the electrolytic reduction of **1**.[48]



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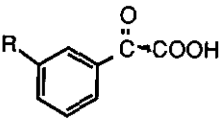
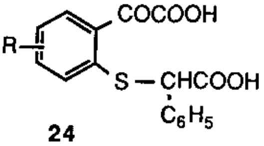
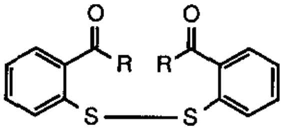


23 R = H, Me



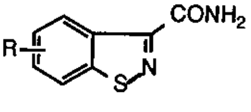
24

Benzo[b]thiophene-2,3-diones undergo oxidation when treated with hydrogen peroxide and ammonia to form, via the imine **12b**, 1,2-benzoisothiazoles **(25)**.[20,49,50,50a] Reaction of **1** with hydrazoic acid in sulfuric acid proceeds to give dimer **26**, presumably via 2-cyanothiophenol.[51] Oxidation of **1** with chloramine T in ethanol results in the formation of **27**.[52]



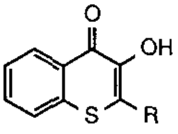
26 R = NH_2

27 R = COOEt



25

Ring expansion reactions of **1** with diazomethane and substituted diazomethane in ether have been reported to give 3-hydroxy-1-thiochromone **(28)** and isomer **29**.[53] In contrast, the formation of methylene ethers, such as **30**, has also been reported from the reaction of **1** and diazomethane in benzene.[54] Compound **30** readily oxidizes in air to give benzo[b]thiophene-2,3-dione.



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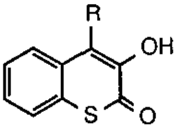

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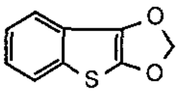

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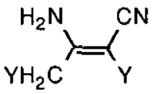
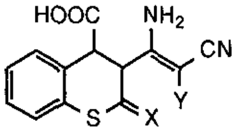


31 · Y = CN

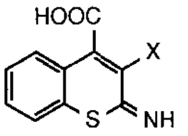
32 Y = COOEt

Ring opening reactions of **1** have also been observed on treatment with **31** in the presence of triethylamine to give **33**,[55] presumably via the cyclization of **12c**. Analogous reaction of **1** with **32** gave **34**.[55] With ethyl cyanoacetate, and in the presence of triethylamine, **1** undergoes ring opening with subsequent cyclization of **12d** to give thiocoumarin derivatives **35** and **37**. Malononitrile and **1** react to give **36** in the presence of triethylamine.[55] Reaction of **1** and malononitrile in the absence of triethylamine gave the condensation product **38** without ring opening.[55] It may be noted that isatin reacts with ethyl cyanoacetate and malononitrile in the presence of diethylamine or piperidine to give simple condensation products.[3] Reaction of **1** with hydrazine hydrate in aqueous alkali gave 2-mercaptophenylacetic acid.[36] Reduction of the β-carbonyl is accompanied by cleavage of the C-S bond.



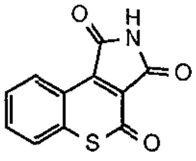
33 X = NH, Y = CN

34 X = O, Y = COOEt



35 X = COOEt

36 X = CN



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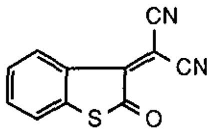

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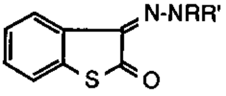
B. Reactions at the carbonyls without ring opening.

Benzo[b]thiophene-2,3-dione undergoes typical carbonyl reactions with ketone reagents. A variety of hydrazines have been reacted with **1** to give hydrazones **(39)** with the condensation taking place at the β-carbonyl.[13,56-63] Thiosemicarbazides and semicarbazides react with **1** at the 3-position to give thiosemicarbazones **(40)** and semicarbazones **(40)**.[49,64-66] The 3-oximes **41** and **42** have also been prepared by reacting **1** with hydroxylamines[67,67a] and N-methylhydroxylamine,[67] respectively.



39

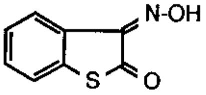
R, R'

Ph, H
Ph, Me
Ph, COMe
H, H
H, Tosyl
H, Me

40

R, R'

H, $CSNH_2$
H, $CONH_2$
H, CSNHMe
H, $C(NH)NH_2$



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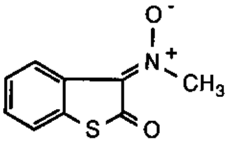
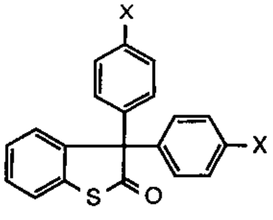


42

In the presence of sulfuric acid, **1** condenses with phenol,[68] thiophenol,[68] N,N-dimethylaniline,[68] aniline,[69,70] and benzene[71] to give **43**, **44**, **45**, **46**, and **47**, respectively. In contrast, the use of a Lewis acid (eg. aluminum chloride) gave the condensation products **(48)** from the reaction of **1** with substituted benzene.[72] Compound **46** has also been synthesized from the condensation of diphenylurea with **1**,[73-75] in the presence of aluminum chloride.



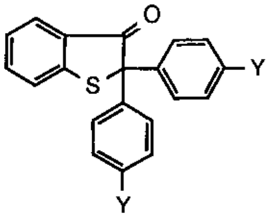
43 X = OH

44 X = SH

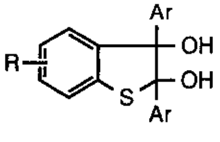
45 $X = N(Me)_2$

46 $X = NH_2$

47 X = H

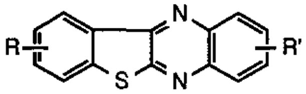


48 Y = Me or OMe



49 Ar = Ph or $PhCH_2$
R = H, 5-Me, 5-Cl, 7-Me

Grignard reagents, such as phenylmagnesium bromide and benzylmagnesium chloride react with benzo[b]thiophene-2,3-dione and **5** (R = 5-methyl, 5-chloro, 7-methyl) at both carbonyls to give 1,2-diols (**49**).[71,72] The analogous reaction of Grignard reagents with isatin has been shown to give 3-hydroxy-3-substituted-indole-2-ones.[3] Condensation of **1** and substituted benzo[b]thiophene-2,3-diones (**5**) with ortho-phenylenediamines have been reported to give thionaphthophenazines (**50**),[76] whereas, non-ortho phenylenediamines react with **1** to give **51**.[77] The analog **52** has been synthesized from **1** and diaminomaleonitrile.[78] Isatin reacts with ortho-aromatic diamines to give indoloquinoxalines. With diaminomaleonitrile isatin forms a Schiff base.[3]



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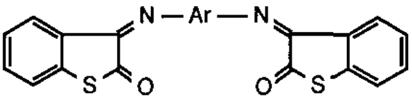

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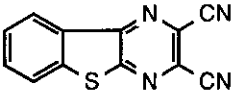

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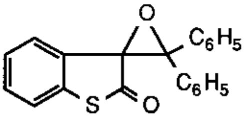

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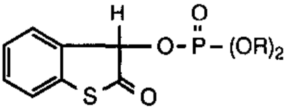
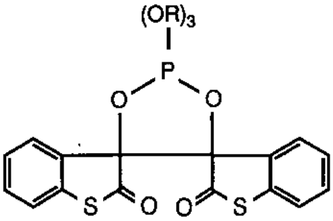


54 R = Me or Et

Reaction of **1** with diphenyldiazomethane in ether gave the epoxide **53**.[79-81] Dimethyl and diethylphosphites react with **1** at the β-carbonyl to give **54**.[79-81] Trialkylphosphites give a dimeric product (**55**).[82] Interestingly,



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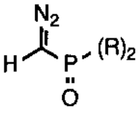
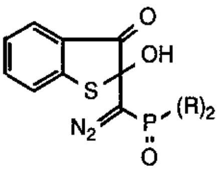


56 R = Ph

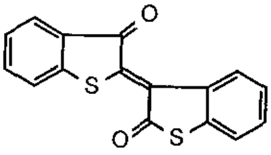
57 R = OMe



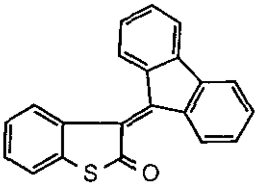
58 R = Ph

59 R = OMe

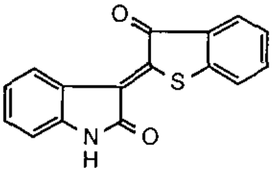
the reaction of **1** with diazomethyl-diphenylphosphine oxide (**56**) or dimethyldiazo-methylphophonate (**57**) occurs at the α-carbonyl to give **58** and **59**, respectively.[83] Triphenylphosphine reacts with **1** to give thioindirubin **60**,[84] and fluorenylidenetriphenyl phosphorane undergoes Wittig reaction at the β-carbonyl to give **61**.[84]



60

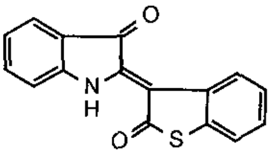


61

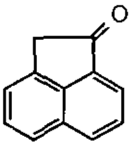


62

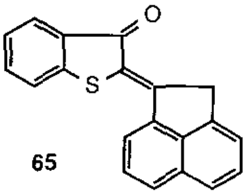
The condensation of **1** and substituted benzo[b]thiophene-2,3-diones (**5**) with active methylene compounds seems to be sensitive to positions of the substituents and solvents. Condensation of **1** with thioindoxyl in glacial acetic acid occurs at the β-carbonyl[85,86] to give **60**. In an alcoholic solution, **1** condenses with thioindoxyl to give **60**,[19,23,24] but a substituent on **1** at the 4-position directs the course of the reaction and



63



64

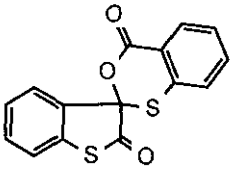


65

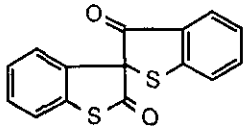
condensation occurs at the α-carbonyl to give **10**.[24] Condensation of **1** with oxindole occurs at the α-position to give **62**, [23] whereas the reaction with indoxyl occurs at the β-carbonyl of **1**,[13,23] to give **63**. Reaction of **1** and **64** results in the formation of **65**.[23] The condensation of **1** with proline has been utilized in the preparation of dyes.[87]

C. Miscellaneous Reactions.

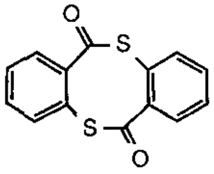
In liquid paraffin and at temperatures above 240° C, **1** undergoes thermolysis to give **66**, **67**, and **68**. In diphenylmethane the thermolysis products are **66**, **67**, and **69**.[81] At 600° C **1** loses a molecule of carbon monoxide to form the thiolactam **70**.[88] Flash vacuum pyrolysis of **1** also resulted in the formation of **70**.[88a] The use of **1** in the Strecker degradation of phenylamino acids into benzaldehyde has been reported.[89]



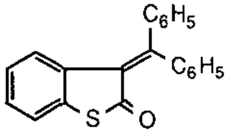
66



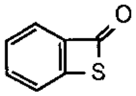
67



68



69



70

Spectral studies which corroborate the structure of **1** have been reported. The ^{13}C nmr,[90-92] infrared,[93] Raman[93] and pmr[94] spectral characteristics of **1** have been reported, as have esr[16,18,95] studies on adducts of **1**. The photoelectron spectral studies of **1** have been reported.[96] The redox potential of **1** has been determined[97] and radical adducts of **1** have been investigated by esr.[98] Theoretical studies of the singlet electronic transitions of **1** have been reported,[77,99] the electric dipole moments of **1** *have been measured and* the electronic spectra discussed.[100]

Benzo[b]thiophene-2,3-dione was found to be inactive in the treatment of hypoxic cells,[101] but was determined to be an inhibitor of polio virus.[51]

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