

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

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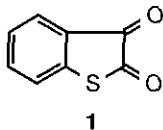
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Abstract—The synthesis and reactions of benzo[b]thiophene-2,3-diones are presented in this review. References to miscellaneous studies on the title compound are also included.

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 Candeia²

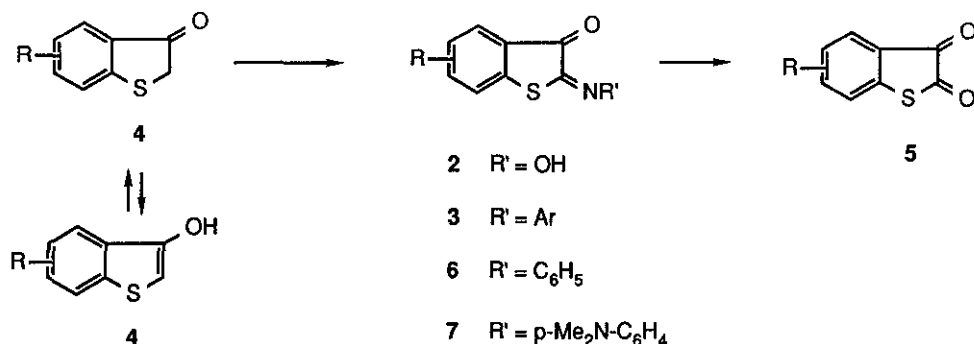


published a review on the development of benzo[b]thiophene-2,3-diones with reference to their chemistry, constitution and properties. Hartough and Meisel have reviewed² the synthesis and chemistry of benzo[b]thiophene-2,3-diones up to 1953. Iddon and Scrowston have discussed² some aspects of the chemistry 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 Sumpter³ and by Popp.³

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.

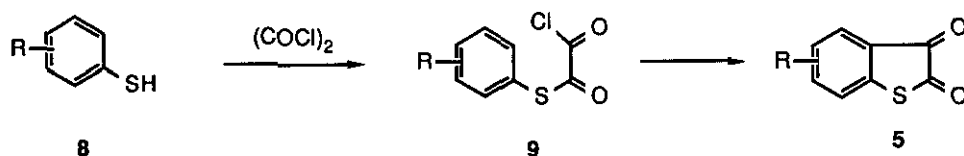
SYNTHESIS OF BENZO[b]THIOPHENE-2,3-DIONES

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



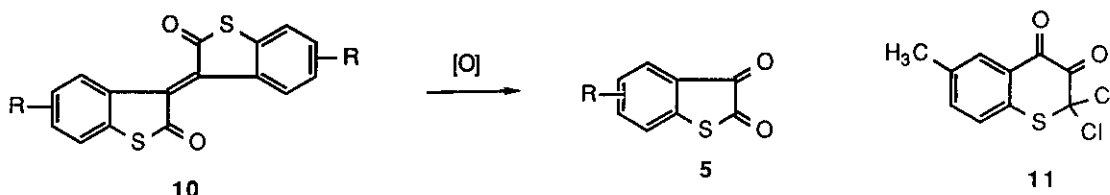
The 2-anils of benzo[b]thiophene-2,3-dione (3) are also prepared from thioindoxyl. Thus, thioindoxyl (4, R = H) has been converted to anil 6 by bromination, and subsequent reaction of the 2,2-dibromobenzo[b]thiophene-3-one with aniline.⁸⁻¹¹ Hydrolysis of 6 using hydrochloric acid furnished 1.⁸⁻¹¹ Another 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-methyl³⁰ 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,



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



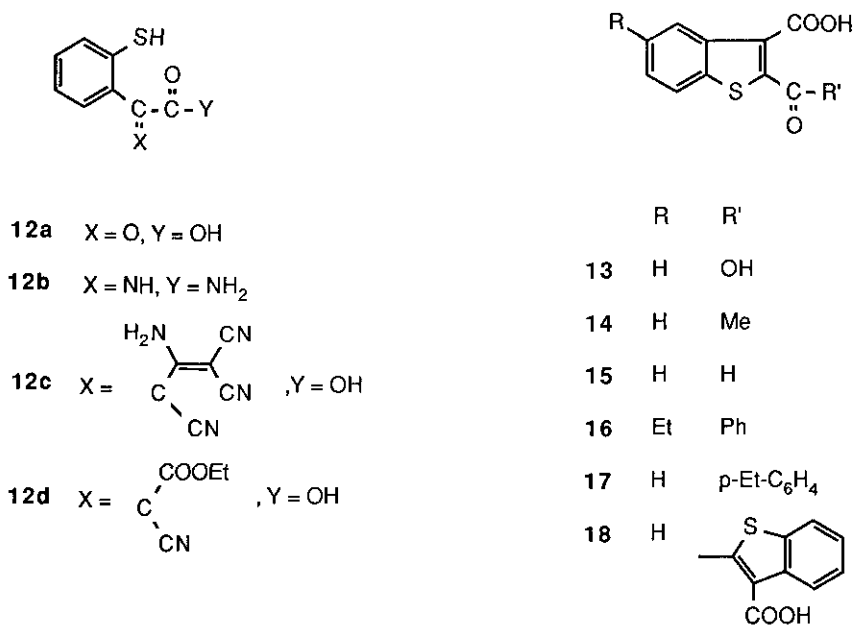
When heated in water, compound **11** has been reported⁴³ to undergo hydrolytic ring opening and subsequent recyclization to give 5-methylbenzo[b]thiophene-2,3-dione. The mechanism for this ring contraction has been discussed.⁴³

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

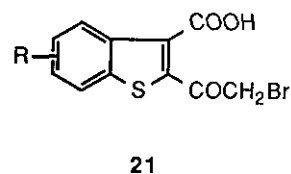
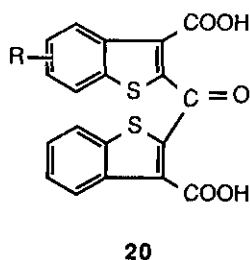
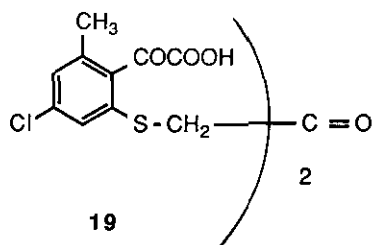
As seen with isatins,³ reactions of benzo[b]thiophene-2,3-diones can be broadly classified into two categories: Reactions that involve ring opening of the heterocycle and reactions involving the carbonyls without cleavage of the C-S bond.

A. Ring opening reactions.

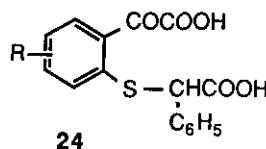
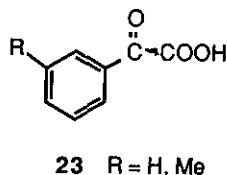
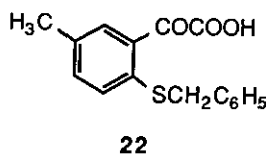
On treatment with alkali, **1** undergoes cleavage of the C-S bond to form 2-mercaptophenyglyoxalic acid (**12a**). Reaction of **12a** with chloroacetic acid in the presence of base gives benzo[b]thiophene-2,3-dicarboxylic acid (**13**).^{8-11,44} 5-Methyl, 5-ethyl, and 6-methoxy analogs of **13** have 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



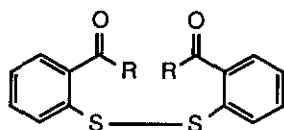
presence of alkali gave the 2-benzoyl analog **16**;¹⁷ and under similar conditions reaction of **1** with 4-ethylphenacyl bromide furnished **17**.¹⁷ Compound **18** was obtained from the reaction of benzo[b]thiophene-2,3-dione (two equivalents) with 1,3-dichloropropanone,⁹ whereas, 6-chloro-4-methylbenzo[b]thiophene-2,3-dione 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}



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

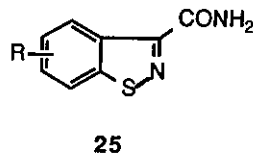


Benzo[b]thiophene-2,3-diones undergo oxidation when treated with hydrogen peroxide and ammonia to form, via the imine **12b**, 1,2-benzisothiazoles (**25**).^{20,49,50,50a} Reaction of **1** with hydrazoic acid in sulfuric acid proceeds to give dimer **26**, presumably via 2-cyanothiophenol.⁵¹ Oxidation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

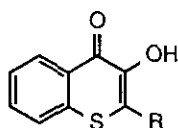


26 R = NH₂

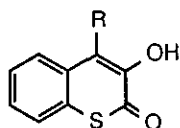
27 R = COOEt



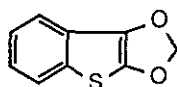
Ring expansion reactions of **1** with diazomethane and substituted diazomethane in ether have been reported to give 3-hydroxy-1-thiochromone (**28**) and isomer **29**.⁵³ In contrast, the formation of methylene ethers, such as **30**, has also been reported from the reaction of **1** and diazomethane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



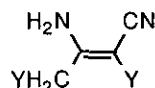
28



29



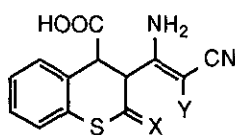
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31 Y = CN

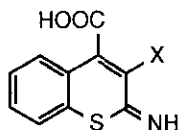
32 Y = COOEt

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.



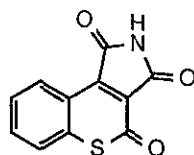
33 X = NH, Y = CN

34 X = O, Y = COOEt

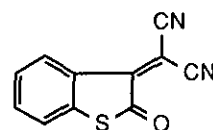


35 X = COOEt

36 X = CN



37

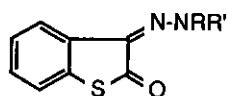


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B. Reactions at the carbonyls without ring opening.

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.

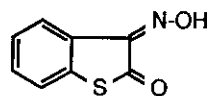
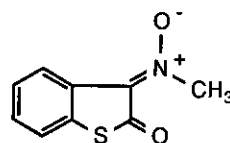

39

R, R'

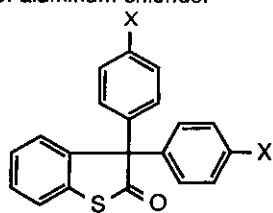
 Ph, H
 Ph, Me
 Ph, COMe
 H, H
 H, Tosyl
 H, Me

40

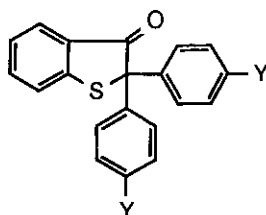
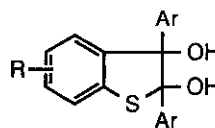
R, R'

 H, CSNH₂
 H, CONH₂
 H, CSNHMe
 H, C(NH)NH₂

41

42

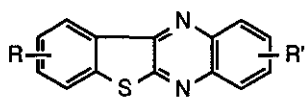
In the presence of sulfuric acid, **1** condenses with phenol,⁶⁸ thiophenol,⁶⁸ N,N-dimethylaniline,⁶⁸ aniline,^{69,70} and benzene⁷¹ to give **43**, **44**, **45**, **46**, and **47**, respectively. In contrast, the use of a Lewis acid (eg. aluminum chloride) gave the condensation products (**48**) from 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

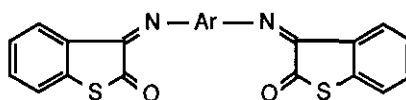
44 X = SH

45 X = N(Me)₂
46 X = NH₂
47 X = H

48 Y = Me or OMe

49 Ar = Ph or PhCH₂
 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

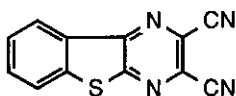


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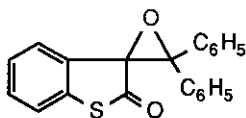


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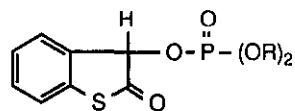
phenylenediamines react with **1** to give **51**.⁷⁷ The analog **52** has been synthesized from **1** and diaminomaleonitrile.⁷⁸ Isatin reacts with ortho-aromatic diamines to give indoloquinolines. With diaminomaleonitrile isatin forms a Schiff base.³



52

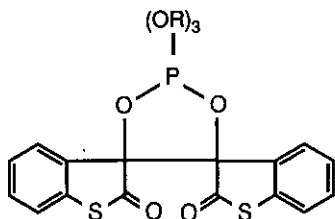


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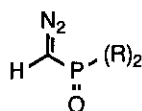


54 R = Me or Et

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,

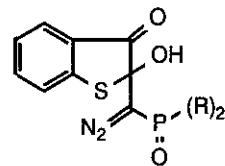


55



56 R = Ph

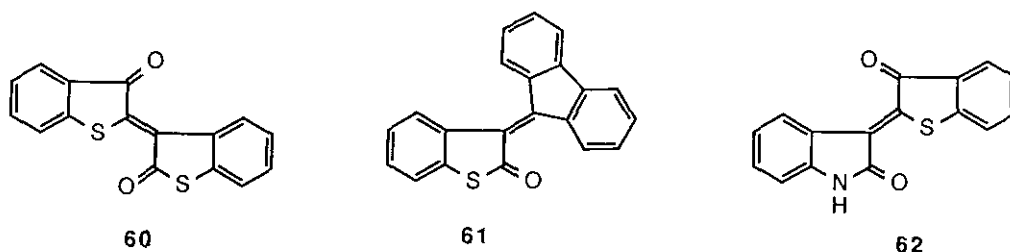
57 R = OMe



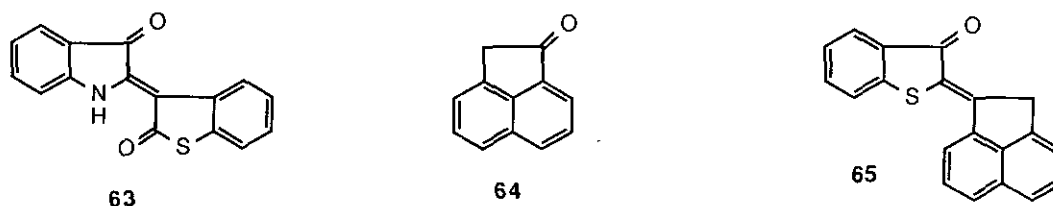
58 R = Ph

59 R = OMe

the reaction of **1** with diazomethyl-diphenylphosphine oxide (**56**) or dimethyldiazo-methylphosphonate (**57**) occurs at the α -carbonyl to give **58** and **59**, respectively.⁸³ Triphenylphosphine reacts with **1** to give thioindirubin **60**,⁹⁴ and fluorenylidetriphenyl phosphorane undergoes Wittig reaction at the β -carbonyl to give **61**.⁸⁴



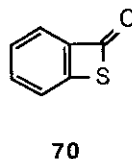
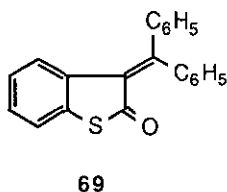
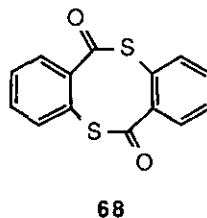
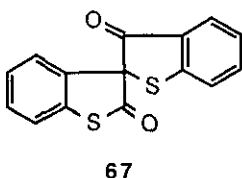
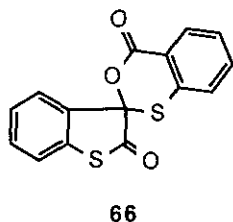
The condensation of **1** and substituted benzo[*b*]thiophene-2,3-diones (**5**) with active methylene compounds seems to be sensitive to positions of the substituents and solvents. Condensation of **1** with thioindoxyl in glacial acetic acid occurs at the β -carbonyl^{85,86} to give **60**. In an alcoholic 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



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



Spectral studies which corroborate the structure of **1** have been reported. The ¹³C nmr,⁹⁰⁻⁹² infrared,⁹³ Raman⁹³ and pmr⁹⁴ spectral characteristics of **1** have been reported, as have esr^{16,19,95} studies on adducts of **1**. The photoelectron spectral studies of **1** have been reported.⁹⁶ The redox potential of **1** has been determined⁹⁷ 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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