The Synthesis of Two Benzo[*c*:*d*']diisothiazoles

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Two benzo[*c*:*d*']diisothiazoles, 8-methylbenzo[1,2-*c*:5,6-*d*']diisothiazole and 3-methylbenzo[1,2-*c*:6,5-*d*']diisothiazole, have been made by reaction of appropriate aminomethyl-1,2-benzisothiazoles with *N*-sulfinylmethanesulfonamide.

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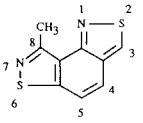
Although some examples of the various benzo[*c*:*c*']diisothiazole systems [1], and a few of the benzo[*d*:*d*']diisothiazole systems [2,3,4], are known, there are no reports of the "mixed", systems, *i.e.* the benzo[*c*:*d*']diisothiazoles. Such compounds would be very useful for comparison of relative reactivities of benzo[*d*]-, and benzo[*c*]isothiazoles. As the former are conveniently made by the cyclization of *o*-alkylthioarylketoximes [2,4-8], and the most convenient synthesis of benzo[*c*]isothiazoles is from *o*-toluidine derivatives by reaction with *N*-sulfinylmethanesulfonamide [9], a suitable approach to some of these compounds appeared to be *via* benzo[*d*]isothiazoles (1,2-benzisothiazoles) containing both amino and methyl groups in *ortho* positions on the aromatic ring.



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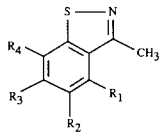
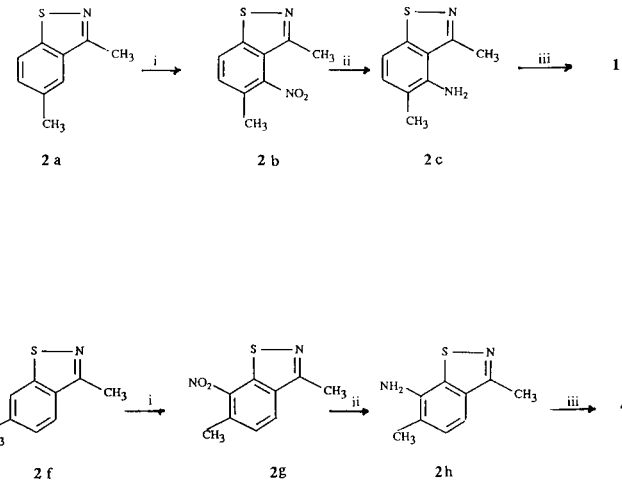


2

a $R_1 = R_3 = R_4 = H$, $R_2 = CH_3$
b $R_1 = NO_2$, $R_2 = CH_3$, $R_3 = R_4 = H$
c $R_1 = R_4 = H$, $R_2 = CH_3$, $R_3 = NO_2$
d $R_1 = R_3 = H$, $R_2 = CH_3$, $R_4 = NO_2$
e $R_1 = NH_2$, $R_2 = CH_3$, $R_3 = R_4 = H$
f $R_1 = R_2 = R_4 = H$, $R_3 = CH_3$
g $R_1 = R_2 = H$, $R_3 = CH_3$, $R_4 = NO_2$
h $R_1 = R_4 = H$, $R_2 = NO_2$, $R_3 = CH_3$

For the synthesis of an example **1** of the benzo[1,2-*c*:6,5-*d*']diisothiazole system, (see Scheme), 3,5-dimethyl-1,2-benzisothiazole (**2a**) was prepared from 5-methyl-2-(methylthio)acetophenone (**3a**), as described [8]. When this was nitrated only one product was obtained. As the ^1H nmr spectrum of this indicated the aromatic protons as two doublets, with a J value of 8 Hz, corresponding to an *ortho* situation, this compound is the 4-nitro-isomer **2b** rather than the 6-, or 7-isomers **2c,d** respectively. As earlier studies on 1,2-benzisothiazoles unsubstituted in the aromatic ring demonstrated that electrophilic substitution is in the 5- or 7-positions [10], in accord with theory [11], it appears that the substituent, even a weakly electron releasing group such as methyl, rather than the heterocyclic ring, determines the product distribution. Bordwell [12] has rationalized the substitution of the somewhat related 5-aminobenzo[*b*]thiophenes on the basis of the contributing resonance structures of intermediate ions, and further to the preference for substitution of naphthalene in the 1-position. Thus a crude comparison of 1,2-benzisothiazoles would be to isoquinolines, and it is found that some 7-substituted isoquinolines do undergo electrophilic substitution in the 8-position, corresponding to the 4-position of the 1,2-benzisothiazole system.

SCHEME Syntheses of benzodiisothiazoles **1** and **4** from benzo[d]isothiazoles.

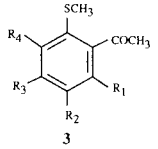


i, HNO_3 , H_2SO_4 ; ii, Fe, HOAc ; iii, N-Sulfinylmethanesulfonamide.

When the nitro compound **2b** was reduced it gave the amine **2e**, and reaction of this with *N*-sulfinylmethanesulfonamide gave the product **1a**. The ^1H nmr spectrum of this compound showed a singlet at 9.26 ppm, typical for the protons in the 3-position of a 2,1-benzisothiazole ring [13,14] confirming the identity of the ring, and the assignment of the substitution pattern in **2b**.

The synthesis of an example of the other system **4** was started from 2-bromo-4-methylbenzoic acid (**5a**) which was converted *via* reaction of its acid chloride with diethyl ethoxymagnesiummalonate and hydrolysis into 2-bromo-4-methylacetophenone (**5b**). Treatment of this with lithium methanethiolate gave 4-methyl-2-(methylthio)acetophenone (**3b**), whose oxime cyclised by treatment with acetic anhydride in pyridine to 3,6-dimethyl-1,2-benzisothiazole

(**2f**). When this was nitrated only one product was isolated. As the ^1H nmr of this material indicated the aromatic protons resonating as two doublets with a J value of 8 Hz, corresponding to an *ortho* situation, this compound is assigned the structure **2g**, *i.e.*, the 7-nitro- and not the less sterically hindered 5-nitro-compound. Previous results [4] of acylation of 1,2-benzisothiazoles indicated a similar substitution pattern. Conversion of this to the amine **2h** and reaction with *N*-sulfinylmethanesulfonamide gave the diisothiazole **4**, (see Scheme). The ^1H nmr spectrum showed a single proton resonating at 9.27 ppm, consistent with its situation at the 3-position of a 2,1-benzisothiazole ring and thus assigned to the 6-proton in **4**. The aromatic protons, two doublets at δ = 7.60 and 7.68 ppm, were assigned to the C-4 and C-5 protons respectively on the basis of their nuclear Overhauser difference spectra from the 3-methyl and C-4 protons.



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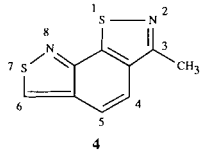
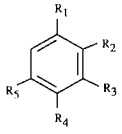


4

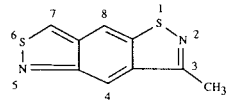
a R_1= R_3= R_4= H , R_2= CH_3

b R_1= R_2= R_4= H , R_3= CH_3

c R_1= R_4= H , R_2= NO_2 , R_3= CH_3



5



6

a R_1= CO_2H , R_2= Br , R_3= R_5= H , R_4= CH_3

b R_1= $COCH_3$, R_2= Br , R_3= R_5= H , R_4= CH_3

c R_1= $COCH_3$, R_2= Cl , R_3= R_5= H , R_4= CH_3

d R_1= $COCH_3$, R_2= Cl , R_3= H , R_4= CH_3 , R_5= NO_2

e R_1= $COCH_3$, R_2= Br , R_3= H , R_4= CH_3 , R_5= NO_2

f R_1= $COCH_3$, R_2= SCH_3 , R_3= H , R_4= CH_3 , R_5= NO_2

g R_1= $COCH_3$, R_2= R_5= SCH_3 , R_3= H , R_4= CH_3

Since it appeared that the ketone **3c** might be a suitable precursor to another member (**6**) of the series, *i.e.* the [1,2-*c*:4,5-*d*'] system, its synthesis from 2-chloro-4-methyl-5-nitroacetophenone has been investigated. Although this compound is reported as the sole product of the Friedel-Crafts acetylation of 3-chlorotoluene [15], more recent work [16] has shown that there are two products produced. As the original authors reported that 2-chloro-4-methyl-5-nitroacetophenone could be made by nitration of this product, the reaction was reinvestigated, as it appeared a less tedious approach to **3c** than *via* the bromoketone **5b**. The acylation reaction did indeed give a mixture of two products, as described [16]. The mixture was then nitrated as described, and from the crude product a reasonably pure compound mp 68-70° was isolated by fractional crystallization. Borsche [15] reported that the mp of this material was 74-76°. Treatment of this compound with one equivalent of lithium methanethiolate in dimethylformamide gave a bright yellow compound whose ^1H nmr spectrum and other data indicated that it was pure, and was the desired 4-methyl-2-methylthio-5-nitroacetophenone (**5f**). This ketone was converted to its oxime under the usual conditions but this failed to give the isothiazole **2h** when treated with acetic anhydride in pyridine. It appears that the nitro group *para* to the methylthio group is not compatible with the cyclization reaction, probably because the nucleophilicity of the sulfur atom is too reduced for successful displacement of the acetoxy group of the oxime acetate intermediate. Although an *ortho* nitro group is compatible with a related cyclisation [17] its effect would be somewhat reduced by steric factors.

In a related reaction, the bromonitroketone **5e**, obtained by nitration of **5b**, underwent displacement of both halogen and nitro groups when treated with an excess of lithium methanethiolate to give **5h**. Several examples of nitro group displacement by thiolate are reported [18], where the nitro group is *ortho*- or *para*- to an alkylthio group.

EXPERIMENTAL

All ^1H nmr spectra were performed in deuteriochloroform solution using tetramethylsilane as an internal standard, and on a Bruker model AM-300 spectrometer. Infrared spectra, obtained on neat samples of oils and in liquid paraffin mulls for solids, were measured on a Perkin-Elmer model 881 spectrometer. Mass spectra were obtained on a VG model 7070E mass spectrometer. Where necessary, solutions were dried over anhydrous magnesium sulfate. Chromatography, unless otherwise stated, was performed on 1 mm thick layers using slicia gel type 60 PF 254 supplied by Merck. The lithium hydroxide used was the monohydrate.

Preparation of 3,5-Dimethyl-4-nitro-1,2-benzisothiazole (**2a**).

2,5-Dimethyl-1,2-benzisothiazole (2.00 g, 0.012 mole) [8], dissolved in sulfuric acid (10 ml), was cooled to −10° and to it was added dropwise a solution of nitric acid (0.77 g, 0.012 moles) in sulfuric acid (1 ml), keeping the temperature below 0°. The mixture was allowed to stand 30 minutes then poured into water and the product collected. It was recrystallized from cyclohexane as pale yellow needles, mp 94-95° (91%). The ^1H nmr spectrum of **2a**, δ = 2.45 ppm (3H, s, *S*-methyl protons), 2.61 (3H, s, 3-methyl protons), 7.42 (1H, d, J = 8 Hz, C-6 protons), 7.89 (1H, d, J = 8 Hz, C-7 protons). The mass spectrum, M Calcd. = 208, M^+ Found = 208, 191 (M^+ -OH). The exact mass Calcd. for $C_9H_8N_2O_2S$ = 208.0306. Found = 208.0292.

Anal. Calcd. for $C_9H_8N_2O_2S$: C, 51.92; H, 3.85; N, 13.46; S, 15.38. Found: C, 52.21; H, 3.61; N, 13.40; S, 15.44.

4-Amino-3,5-dimethyl-1,2-benzisothiazole (**2e**).

To a mixture of 4-nitro-3,5-dimethyl-1,2-benzisothiazole (0.52

g, 2.5 mmoles) in acetic acid (10 ml) and water (2.5 ml) was added iron powder (0.5 g) and the mixture heated at 100° for 3 hours. The mixture was filtered, diluted with water and extracted with chloroform. Evaporation of the extract gave a solid which was crystallized from cyclohexane as yellow needles, mp 120-122° (82%). The ^{1}H nmr spectrum of **2e**, δ = 2.20 ppm (3H, s, 5-methyl protons), 2.86 (3H, s, 3-methyl protons), 4.30 (2H, bs, amino protons), 7.10 (2H, s, aromatic protons). The mass spectrum, M Calcd. = 178, M$^+$ Found = 178, 149 (M$^+$ -NH_2, CH_3).

Anal. Calcd. for $C_9H_{10}N_2S$: C, 60.67; H, 5.62; N, 15.73; S, 17.98. Found: C, 60.83; H, 5.49; N, 15.36; S, 17.69.

8-Methylbenzo[1,2-*c*:6,5-*d'*]diisothiazole (**1**).

To a cooled solution of 4-amino-3,5-dimethyl-1,2-benzisothiazole (**2e**) (0.35 g, 2 mmoles) in dry benzene (10 ml), was added a solution of *N*-sulfinylmethanesulfonamide (0.42 g, 3.0 mmoles) [9] in dry benzene (1 ml). Pyridine (0.237 g, 3.0 mmoles) in benzene (1 ml) was then added to the chilled mixture. A solid precipitate formed on this addition. After heating under reflux for 18 hours with stirring, the benzene and pyridine were removed under reduced pressure and the residue was treated with water (35 ml) and let stand for 30 minutes. The mixture was extracted with chloroform and the dried extract was evaporated to give a solid material which was purified by chromatography using a benzene:chloroform 1:1 mixture as an eluent. The compound was recrystallized from cyclohexane as colorless needles, mp 142-144° (26%). The ^{1}H nmr spectrum of **1a**, δ = 3.21 ppm (3H, s, 3-methyl protons), 7.67 (1H, d, J = 9 Hz, C-8 proton), 7.76 (1H, d, J = 9 Hz, C-7 proton), 9.26 (1H, s, C-6 proton). The mass spectrum, M Calcd. = 206, M$^+$ Found = 206. The exact mass Calcd. for $C_9H_6N_2S_2$ = 205.9972. Found = 205.9985.

Anal. Calcd. for $C_9H_6N_2S_2$: C, 52.43; H, 2.91; N, 13.59; S, 31.07. Found: C, 52.71; H, 2.98; N, 13.38; S, 31.03.

2-Bromo-4-methylbenzoic Acid (**5a**).

This was prepared as described [19] from 2-bromo-4-methylbenzonitrile prepared by the method of Lindemann [20].

2-Bromo-4-methylacetophenone (**5b**).

2-Bromo-4-methylbenzoyl chloride (17.00 g, 0.07 mole), prepared by reaction of the acid **5a** with thionyl chloride, in benzene (50 ml), was added to a benzene (60 ml) solution of diethyl ethoxymagnesiummalonate (prepared from magnesium (3.85 g, 0.16 mole) and ethanol (25 ml) and diethyl malonate (25.54 g, 0.16 mole)). The mixture was let stand 16 hours, then acidified, and the benzene layer separated, and evaporated. The resulting oil was hydrolysed in a boiling mixture of acetic acid (60 ml), concentrated sulfuric acid (2 ml) and water (16 ml) until there was no further gas evolution. Work up gave a yellow oil which was distilled under reduced pressure, bp = 80° at 1 mm, lit [21] = 130° at 12 mm. The ^{1}H nmr spectrum of **5b**, δ = 2.33 ppm (3H, s, aromatic methyl), 2.58 (3H, s, acetyl protons), 7.10 (1H, d, J = 6.9 Hz, C-5 proton), 7.34 (1H, bs, C-3 proton), 7.41 (1H, d, J = 6.9 Hz, C-6 proton). The mass spectrum, M Calcd. = 214, 212. M$^+$ Found = 214, 212.

4-Methyl-2-(methylthio)acetophenone (**3b**).

To a solution of 2-bromo-4-methylacetophenone (5 g, 0.023 mole), and methanethiol (5 ml) in dimethyl formamide (50 ml), under a nitrogen atmosphere, lithium hydroxide (5 g) was added portionwise. The mixture was stirred at 30° for 30 minutes and then poured into ice water and acidified with dilute hydrochloric acid. The mixture was extracted with chloroform which was dried and evaporated to give a yellow oil. This was purified by chromatography using chloroform as an eluent, giving the ketone as a yellow oil (85%). The ^{1}H nmr spectrum of **3b**, δ = 2.33 ppm (6H, s, *S*-methyl and aromatic protons), 2.50 (3H, s, acetyl methyl protons), 6.93 (1H, d, J = 9 Hz, C-5 proton), 7.03 (1H, bs, C-3 proton), 7.70 (1H, d, J = 9 Hz, C-6 proton). The ir spectrum, 1692 cm^{-1} (C=O str). The mass spectrum, M Calcd. = 180, M$^+$ Found = 180, 165 (M$^+$ -CH_3).

Anal. Calcd. for $C_{10}H_{12}SO$: C, 66.67; H, 6.67; S, 17.78. Found: C, 66.51; H, 6.88; S, 18.02.

3,6-Dimethyl-1,2-benzisothiazole (**2f**).

The ketone **3b**, (2.50 g, 0.014 mole) in methanol (10 ml) with pyridine (3 ml) and hydroxylamine hydrochloride (1 g) was heated under reflux 18 hours. The mixture was acidified with dilute hydrochloric acid and the oxime was extracted with chloroform. Evaporation gave a yellow paste which was dissolved in a mixture of pyridine (10 ml) and acetic anhydride (4 ml) and heated under reflux 24 hours. This mixture was diluted with dil. hydrochloric acid and extracted with chloroform. This extract was dried and evaporated to give a yellow oil which was distilled, bp = 258° (88%). The ^{1}H nmr spectrum of **2f**, δ = 2.50 ppm (3H, s, 6-methyl protons), 2.71 (3H, s, 3-methyl protons), 7.23 (1H, d, J = 8.1 Hz, C-5 proton), 7.73 (1H, bs, C-7 proton), 7.80 (1H, d, J = 8.1 Hz, C-4 proton). The mass spectrum, M Calcd. = 163, M$^+$ Found = 163, 148 (M$^+$ -CH_3).

Anal. Calcd. for C_9H_9NS: C, 66.26; H, 5.52; N, 8.59; S, 19.60. Found: C, 66.38; H, 5.29; N, 8.60; S, 19.88.

3,6-Dimethyl-7-nitro-1,2-benzisothiazole (**2g**).

This was made as for the preparation of **2a** above, starting from **2f**. The product was recrystallized from ethanol as pale yellow needles, mp 143° (89%). The ^{1}H nmr spectrum of **2g**, δ = 2.77 ppm (3H, s, 6-methyl protons), 2.96 (3H, s, 6-methyl protons), 2.96 (3H, s, 3-methyl protons), 7.47 (1H, d, J = 8 Hz, C-5 proton), 8.08 (1H, d, J = 8 Hz, C-4 proton). The mass spectrum, M Calcd. 208. M$^+$ Found = 208, 191 (M$^+$ -OH). The exact mass, Calcd. for $C_9H_8N_2O_2S$ = 208.0306. Found = 208.0306.

Anal. Calcd. for $C_9H_8N_2O_2S$: C, 51.92; H, 3.85; N, 13.46; S, 15.38. Found: C, 51.89; H, 3.82; N, 13.60; S, 15.44.

7-Amino-3,6-dimethyl-1,2-benzisothiazole (**2h**).

7-Nitro-3,6-dimethyl-1,2-benzisothiazole was reduced as for the preparation of **2e**. The amine **2b** was obtained as yellow needles, mp 215-219° from a benzene:cyclohexane 1:1 mixture (83%). The ^{1}H nmr spectrum of **2b**, δ = 2.33 ppm (3H, s, 6-methyl protons), 3.72 (3H, s, 3-methyl protons), 3.92 (2H, bs, amino protons), 7.20, 7.31 (two 1H, d, J = 9 Hz, 4 and 5 aromatic protons). The mass spectrum M Calcd. = 178, M$^+$ Found = 178, 163 (M$^+$ -CH_3).

Anal. Calcd. for $C_9H_{10}N_2S$: C, 60.67; H, 5.62; N, 15.73; S, 17.98. Found: C, 60.78; H, 5.81; N, 16.01; S, 18.10.

3-Methylbenzo[1,2-*c*:6,5-*d'*]diisothiazole (**4**).

To a cooled solution of the amine **2h** (0.3 g, 1.6 mmoles) in dry benzene (5 ml) was added a solution of *N*-sulfinylmethanesulfonamide (0.24 g, 1.7 mmoles) in benzene (2 ml) followed by a solution of pyridine (0.14 g, 1.7 mmoles) in benzene (2 ml). The mixture was heated under reflux for 18 hours with stirring, then the solvents were removed under reduced pressure. The residue was

digested with water (5 ml) and extracted with chloroform. The dried extract was evaporated to give a solid which was purified by chromatography on silic gel using a benzene:chloroform 1:1 mixture as an eluent. The compound was obtained as colorless prisms mp 205-207° (40%). The ^{1}H nmr spectrum of **4**, δ = 2.80 ppm (3H, s, the methyl protons), 7.60 (1H, d, J = 9 Hz, C-4 proton), 7.68 (1H, d, J = 9 Hz, C-5 proton), 9.25 (1H, s, C-6 proton). The positions of these were confirmed by nuclear Overhauser difference spectra. The mass spectrum, M Calcd. = 206, M^+ Found = 206, 191 (M^+ -CH_3). The exact mass, Calcd. for $C_9H_6N_2S_2$ = 205.9972. Found = 205.9969.

Anal. Calcd. for $C_9H_6N_2S_2$: C, 52.43; H, 2.91; N, 13.59; S, 31.07. Found: C, 52.35; H, 3.04; N, 13.73; S, 30.85.

Preparation of 2-Chloro-4-methyl-5-nitroacetophenone (**5d**).

The product of acetylation of 3-chlorotoluene [16] was nitrated as described [15]. When the nitration mixture was poured over ice water a pasty solid was obtained. Fractional crystallization from ethanol gave **5d** as long fibrous needles mp 68-70°, lit [15] 74-76° (21%). The nmr spectrum of this indicated that it was only about 80% pure.

4-Methyl-2-methylthio-5-nitroacetophenone (**5f**).

To a stirred solution of the crude ketone **5d** from above, (2.27 g, 0.01 mole) in dimethyl formamide (20 ml) with lithium hydroxide (0.41 g, 0.01 mole) was added liquid methanethiol (1 ml). The mixture slowly turned yellow and after 2 hours a yellow precipitate had formed. After 16 hours the mixture was diluted with water and the precipitate collected. It was recrystallized from ethanol as lemon yellow needles, mp 145° (61%). The ^{1}H nmr spectrum of **5f**, δ = 2.55 ppm (3H, s, aromatic of *S*-methyl protons), 2.70 (6H, s, acetyl and *S*-methyl or aromatic methyl protons), 7.39 (1H, s, C-3 proton), 8.73 (1H, s, C-6 proton). The ir spectrum, 1691 cm^{-1} (C=O str). The mass spectrum, M Calcd. = 225, M^+ Found = 225, 210 (M^+ -CH_3).

Anal. Calcd. for $C_{10}H_{11}NO_3S$: C, 53.33; H, 4.89; N, 6.22; S, 14.22. Found: C, 53.36; H, 4.99; N, 6.03; S, 14.07.

2-Bromo-4-methyl-5-nitroacetophenone (**5e**).

To a solution of 2-bromo-4-methylacetophenone (**5b**) (6.30 g, 0.03 mole) in concentrated sulfuric acid (30 ml) was added dropwise a mixture of concentrated sulfuric acid (5 ml) and fuming nitric acid (1.9 ml, 0.03 mole), keeping the temperature below 5°. The mixture was stirred 2 hours, then poured into ice water and extracted with chloroform. The dried chloroform solution was evaporated to give a semi-crystalline solid which was purified by chromatography, using chloroform as an eluent. Pale yellow needles, mp 63°, were obtained (92%). The ^{1}H nmr spectrum of **5e**, δ = 2.67 ppm (3H, s, 4-methyl protons), 2.73 (3H, s, acetyl protons), 7.74 (1H, s, C-3 proton), 8.25 (1H, s, C-6 proton). The mass spectrum, M Calcd. = 257, M^+ Found = 257, 242 (M^+ -CH_3), 227 (M^+ -$2CH_3$). The ir spectrum, 1697 cm^{-1} (C=O str).

Anal. Calcd. for $C_9H_8BrNO_3$: C, 41.86; H, 3.10; Br, 31.01; N, 5.42. Found: C, 42.20; H, 3.26; Br, 30.69; N, 5.38.

4-Methyl-2,5-bis(methylthio)acetophenone (**5g**).

To a solution of 2-bromo-4-methyl-5-nitroacetophenone (**5e**), (7.00 g, 0.027 mole) and methanethiol (10 ml) in dimethylformamide (80 ml) was added portionwise lithium hydroxide (10 g). The reaction mixture was stirred 30 minutes at 30°, then poured into ice water and extracted with chloroform. The dried extract was evaporated to give a yellow solid which crystallized from benzene as yellow prisms, mp 130-133° (80%). The ^{1}H nmr spectrum of **5g**, δ = 2.50 ppm (3H, s, aromatic methyl protons), 2.70 (6H, s, *S*-methyl protons), 2.74 (3H, s, acetyl protons), 7.20 (1H, s, C-3 proton), 8.63 (H, s, C-6 proton). The mass spectrum, M Calcd. = 226, M^+ Found = 226, 211 (M^+ -CH_3), 196 (M^+ -$2CH_3$). The ir spectrum, 1676 cm^{-1} (C=O str).

Anal. Calcd. for $C_{11}H_{14}OS_2$: C, 58.41; H, 6.19; S, 28.32. Found: C, 58.15; H, 6.27; S, 28.09.

Attempted Preparation of 3,6-Dimethyl-5-nitro-1,2-benzisothiazole (**2h**).

The ketone **5g** (0.258 g, 1.0 mmole) was treated with hydroxylamine hydrochloride and then with acetic anhydride in pyridine as described for **2f**. Work up only afforded as small amount (~20 mg) of an amorphous material which was not further examined.

Acknowledgements.

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