The Synthesis of some Benzo[*d,d'*]diisothiazoles

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Four examples of benzo[*d,d'*]diisothiazoles have been made by cyclisation of appropriate *o*-alkylthioarylketoximes by simultaneous or consecutive ring formation.

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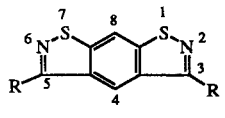
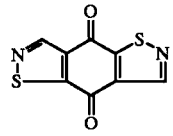
Although a number of fused benzo[*c,c'*]diisothiazoles have been made [1], there is only one report [2] of a benzo[*d,d'*]diisothiazole (*i.e.* the benzo[1,2-*d*:5,4-*d'*] system **1**, although a quinone derivative of the benzo[1,2-*d*:4,5-*d'*]-diisothiazole system **3** has been made by the double addition of a "nitrile sulfide" to a quinone [3]. This paper will describe the syntheses of some dimethyl derivatives of these and two other systems, the [1,2-*d*:6,5-*d'*] system **4**, and the [1,2-*d*:3,4-*d'*] system **5**. These syntheses are based on the cyclisation of *o*-alkylthioarylketoximes which have been shown [4-7] to be conveniently converted into 1,2-benzisothiazoles. The acetic anhydride method [7] is especially convenient.



1

a R = H
b R = CH_3



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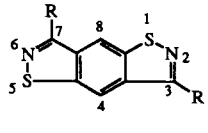
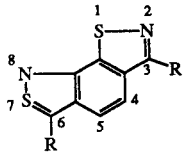


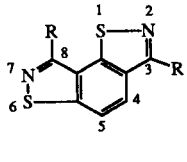
3

a R = H
b R = CH_3



4

a R = H
b R = CH_3



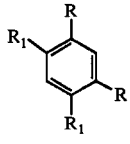
5

a R = H
b R = CH_3

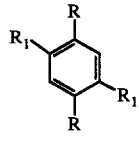
The dimethyl examples of the [1,2-*d*:5,4-*d'*] and [1,2-*d*:-4,5-*d'*] systems, **1b** and **3d** respectively, were approached in similar ways, *i.e.* starting from the appropriate dichloroxylenes **6a** and **7a** respectively. These were oxidized to the corresponding diacids **6b**,**7c** respectively and converted *via* their acid chlorides into the diketones **6c**, **7c** by treatment with diethyl ethoxymagnesiummalonate and hydrolysis. The electron withdrawing substituents now permitted nucleophilic displacement of halogen by methanethiolate ion using the method of Beck [8], giving the bismethylthiodiketones, **6d**, **7d** respectively. Conversion of these to the dioximes **6e**, **7e** respectively and cyclisation gave the benzodiisothiazoles **1b**, **3b** respectively.

A similar approach was used for the system **4**, which required the preparation of dichloroxylene **8a** as a starting material. This compound had been synthesized by Wahl [9], but by a long procedure starting from 2,5-dimethylaniline, and a different method was sought. Thus 2-chloro-1,3-dimethylbenzene (**9a**) was converted to 4-chloro-2,5-dimethylbenzenesulfonic acid (**9b**). Although Wahl reported that 2,5-dimethylbenzenesulfonic acid could not be chlorinated, the acid **9b** chlorinated in sulfuric acid at 60°, presumably giving 3,4-dichloro-2,5-dimethylbenzenesulfonic acid, as hydrolysis and steam distillation of the reaction mixture afforded 2,3-dichloro-1,4-dimethylbenzene (**8a**). This was converted to the acid **9b** and thence to the dichlorodiketone **9c**, which on treatment with lithium methanethiolate gave the diketone **9d**. This was converted *via* its oxime into the benzodiisothiazole **4b**.

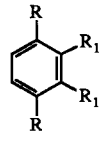
While the δ values for the acetyl- and thiomethyl protons in **9d**, at 2.07 ppm and 1.60 ppm respectively, are considerably outside their normal range, *eg.* those for acetophenone are at 2.53 ppm and those for thioanisole are at 2.45 ppm respectively, this may reflect the lack of planarity of the system and the change in conjugative or deshielding effects. This is consistent with the carbonyl stretching frequency in **9d** of 1700 cm^{-1}. In compounds **7d** and **8d** the frequency is lower by approximately 20 cm^{-1}.



6

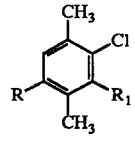


7



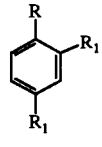
8

a R = CH_3, R_1 = Cl
b R = CO_2H, R_1 = Cl
c R = $COCH_3$, R_1 = Cl
d R = $COCH_3$, R_1 = SCH_3
e R = $CNOH{\cdot}CH_3$, R_1 = SCH_3



9

a R = H, R_1 = H
b R = SO_3H, R_1 = H
c R = SO_3H, R_1 = Cl



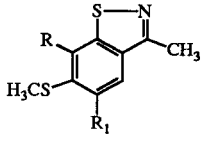
10

a R = $COCH_3$, R_1 = Cl
b R = $COCH_3$, R_1 = SCH_3
c R = $CNOH{\cdot}CH_3$, R_1 = SCH_3

For the synthesis of the system **5**, 2,4-dichloroacetophenone (**10c**) was converted by lithium methanethiolate into the ketone **10d**, and by its oxime to 3-methyl-6-methylthio-1,2-benzisothiazole (**11a**). This compound successfully acetylated under Friedel-Crafts conditions to form **11b**. It thus appears that the alkylthio-group sufficiently activates the ring to acylation despite the electron withdrawing heterocyclic ring. The acylated compound had a ^{1}H nmr spectrum whose aromatic protons had a coupling of J = 9 Hz, *i.e.* a typical *ortho* coupling, indicating that this was the 7-acetyl-compound **11b**, and not the less sterically hindered 5-acetyl compound **11c**. Previous studies [10] had indicated that electrophilic substitution in the 5- and 7-positions is favored, in accord with theoretical predictions [11]. If the intermediate ions for the electrophilic substitution in the 5- or 7-positions are considered then each of these has three resonance structures, ignoring any d-orbital contributors. For the substitution in the 7-position the aromaticity of the isothiazole ring is retained in only one of them. Similar arguments on intermediate stability have been advanced to explain substitution preferences in benzo[*b*]thiophene derivatives [12].

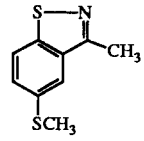
The oxime **11d** of the ketone **11b** successfully cyclised to the dimethylbenzodiisothiazole **5b**. The ^{1}H nmr of this compound, which has two methyl groups, indicating its lack of symmetry, also confirms the position of the acylation above.

Nevertheless, the position of the methylthio-group appears to be important in the success of the acylation reaction. For example, 3-methyl-5-methylthio-1,2-benzisothiazole (**12**) failed to acylate in an attempted synthetic scheme towards the [1,2-*d*:4,3-*d'*] system **13**. In contrast to the compound **11a**, one of the sulfur atoms here would *meta* to any introduced substituent. Scrowston and coworkers report that several 5-substituted 1,2-benzisothiazoles are unreactive to Friedel-Crafts acylation [13]. Compound **12** was made as follows. 2-Methylthiobenzoic acid (**14a**) reacted with chlorosulfonic acid to form the sulfonyl chloride **14b**. Reduction to the mercaptan **14c** and methylation gave 2,5-bismethylthiobenzoic acid (**14d**). Conversion *via* the acid chloride to the ketone **14e** by the method used for **6c** and **7c** and cyclisation of its oxime afforded the isothiazole **12**.

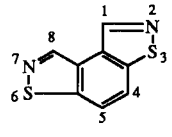


11

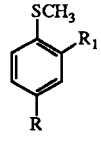
a R = H, R_1 = H
b R = $COCH_3$, R_1 = H
c R = H, R_1 = $COCH_3$
d R = CNOH•CH_3, R_1 = H



12



13



14

a R = H, R_1 = CO_2H
b R = SO_2Cl, R_1 = CO_2H
c R = SH, R_1 = CO_2H
d R = SCH_3, R_1 = CO_2H
e R = SCH_3, R_1 = $COCH_3$
f R = SCH_3, R_1 = CNOH•CH_3

EXPERIMENTAL

All ^{1}H nmr spectra were performed in deuteriochloroform solution using tetramethylsilane as an internal standard, and on a Bruker model AM-300 spectrometer. Infra-red spectra, obtained on neat samples for 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 silica gel type 60 PF 254 supplied by Merck. Lithium hydroxide used was the monohydrate.

Dichlorobenzenedicarboxylic Acids **6b**, **7b** and **8b**.

These were prepared by oxidation of the appropriate dichloroxylenes **6a**, **7a** and **8a**, respectively with potassium permanganate in water. Removal of manganese dioxide by filtration, decolorization with bisulfite and acidification gave the dichlorodiacids which were collected. For **6b**, the yield = 52%, mp 280°, lit [14] 280°. For **7a**, the yield = 45%, mp 306°, lit [15] 306°. For **8a**, the yield = 58%, mp 238°, lit [16] 238°.

4,6-Dichloro-1,3-diacetylbenzene (**6c**).

The acid **7a** (7.00 g, 0.03 mole) was converted to its chloride by reaction with an excess of thionyl chloride (10 ml) in refluxing benzene (30 ml) solution for 24 hours. By this time all the acid had dissolved. The solvent and excess reagent were evaporated under reduced pressure, the acid chloride was redissolved in benzene (20 ml) and added to a solution of diethyl ethoxymagnesiummalonate, prepared from magnesium (2.16 g, 0.09 g-atom), ethanol (3 moles) and diethyl malonate (14.4 g, 0.09 mole) in benzene (30 ml). The mixture was allowed to stand at room temperature for 16 hours, then it was acidified with 10% sulfuric acid (100 ml). The benzene layer was separated, evaporated and the crude ketoester heated under reflux with a solution of sulfuric acid (2 ml) in water (8 ml) and acetic acid (20 ml) until there was no more gas evolution. The mixture was poured onto ice water and the crystalline precipitate collected. The product was recrystallized from acetone as pale yellow needles, mp 50-51°, (96%); ^{1}H nmr: δ = 2.62 (6H, s, methyls), 7.80 (1H, s, H5), 8.02 (1H, s, H2); ir: 1670 cm^{-1} (C=O str); ms: M calcd. = 230. Found: M^+ = 230, 215 (M^+ -CH_3). The exact mass Calcd. for $C_{10}H_8{}^{35}Cl_2O_2$, 229.9991. Found: 229.9898. Calcd. for $C_{10}H_8{}^{35}Cl^{37}ClO_2$, 231.9871. Found: 231.9867.

Anal. Calcd. for $C_{10}H_8Cl_2O_2$: C, 51.95; H, 3.46; Cl, 30.76. Found: C, 52.06; H, 3.39; Cl, 30.55.

1,4-Diacetyl-2,5-dichlorobenzene (**7c**).

This compound was prepared as above starting from acid **8a**. The product was recrystallized from benzene as colorless plates,

mp 99-102° (94%); ^{1}H nmr: δ = 2.70 (6H, s, methyls), 7.62 (2H, s, aromatic); ir 1700 cm^{-1} (C=O str); ms: M calcd. = 230. Found: M$^+$ = 230, 215 (M$^+$ -CH_3). The exact mass Calcd. $C_{10}H_8{}^{35}Cl_2O_2$, 229.9901. Found: 229.9890. Calcd. for $C_{10}H_8{}^{35}Cl^{37}ClO_2$, 231.9871. Found: 231.9850.

Anal. Calcd. for $C_{10}H_8Cl_2O_2$: C, 51.95; H, 3.46; Cl, 30.76. Found: C, 51.83; H, 3.28; Cl, 30.68.

1,4-Diacetyl-2,3-dichlorobenzene (**8c**).

This compound was prepared as above starting from the acid **8b**. The product was a pale yellow oil (94%). It appeared to decompose on attempted distillation and was therefore used without further purification; ^{1}H nmr: δ = 2.60 (6H, s, methyls), 7.40 (2H, s, aromatic); ir 1690 cm^{-1} (C=O str); ms: M Calcd. = 230. Found: M$^+$ = 230, 215 (M$^+$ -CH_3).

4-Chloro-2,5-dimethylbenzenesulfonic Acid (**9b**).

2-Chloro-1,3-dimethylbenzene (**9a**) (50 g, 0.36 mole) in concentrated sulfuric acid (100 ml), was heated under a gentle reflux for 4 hours. The mixture was cooled, poured over ice water, and the product collected, mp 99°, lit [9] 100°. Recrystallization from benzene gave a product mp 90-92°, presumably the anhydrous form; ms: ^{1}H M Calcd. = 222, 220. Found: M$^+$ = 222, 220. The material was insufficiently soluble in chloroform for an ^{1}H nmr spectrum.

2,3-Dichloro-1,4-dimethylbenzene (**8a**).

The sulfonic acid derivative above, **9b** (33.5 g, 0.15 mole) in sulfuric acid (20 ml) was warmed to 60° and gaseous chlorine passed in until the weight had increased by 5.25 g, corresponding to the addition of one equivalent of chlorine. The mixture was then carefully diluted with water and steam distilled until no more oily material came over. The dichloro compound **8a** was obtained as a pale yellow liquid, bp 230°, lit [9], 230°. The product was identical (nmr, ms) to an authentic sample.

4,6-Bismethylthio-1,3-diacetylbenzene (**6d**).

To a cold solution of the diketone **6c** (3.45 g, 0.015 mole) in dimethylformamide (80 ml) with methanethiol (8 ml), was added portionwise lithium hydroxide (10 g). The mixture was stirred for 30 minutes then poured into ice cold 10% hydrochloric acid. The solid product was collected and recrystallized from nitromethane as yellow prisms, mp 209-210° (95%); ^{1}H nmr: δ = 2.51 (6H, s, S-methyls), 2.70 (6H, s, acetyl methyls), 7.12 (1H, s, H5), 8.03 (1H, s, H2); ir: 1670 cm^{-1} (C=O str); ms: M Calcd. = 254. Found: M$^+$ = 254, 239 (M$^+$ -CH_3). The exact mass Calcd. for $C_{12}H_{14}O_2S_2$, 254.0435. Found: 254.0450.

Anal. Calcd. for $C_{12}H_{14}O_2S_2$: C, 56.69; H, 5.51; S, 25.20. Found: C, 56.81; H, 5.53; S, 25.06.

2,5-Bismethylthio-1,4-diacetylbenzene (**7d**).

This compound was prepared as above from **7c**. The compound was obtained as yellow needles, mp 203° from nitromethane, (89%); ^{1}H nmr: δ = 2.50 (6H, s, S-methyls), 2.71 (6H, s, acetyls), 7.72 (2H, s, aromatic); ir: 1680 cm^{-1} (C=O str); ms: M Calcd. 254. Found: M$^+$ = 254, 239 (M$^+$ -CH_3). The exact mass Calcd. for $C_{12}H_{14}O_2S_2$, 254.0435. Found: 254.0427.

Anal. Calcd. for $C_{12}H_{14}O_2S_2$: C, 56.67; H, 5.51; S, 25.20. Found: C, 56.51; H, 5.25; S, 25.04.

2,3-Bismethylthio-1,4-diacetylbenzene (**8d**).

This compound was prepared as above from **8c**, except that the product was extracted from the aqueous mixture with chloroform. The dried solution was evaporated giving the diketone as an orange-yellow oil. It distilled as a yellow oil, bp 180-183° at 0.1 mm, (79%); ^{1}H nmr: δ = 1.60 (6H, s, S-methyls), 2.07 (6H, s, acetyls), 7.40 (2H, s, aromatic); ir: 1700 cm^{-1} (C=O str); ms: M Calcd. = 254. Found: M$^+$ = 254, 239 (M -CH_3). The exact mass Calcd. for $C_{12}H_{14}O_2S_2$. Found: 254.0426.

Anal. Calcd. for $C_{12}H_{14}O_2S_2$: C, 56.69; H, 5.51; S, 25.20. Found: C, 56.81; H, 5.77; S, 25.14.

Preparation of 2,4-bismethylthioacetophenone (**10d**).

This compound was prepared as for the methylthioketones above, starting from 2,4-dichloroacetophenone (**10c**). The product was collected and recrystallized from a benzene:cyclohexane 50:50 mixture as colorless needles, mp 83°, (93%); ^{1}H nmr: δ = 2.43, 2.53 (two 3H, s, S-methyls), 2.57 (3H, s, acetyls), 6.93 (1H, d, J = 9.0 Hz, H5), 7.06 (2H, bs, H3), 7.86 (1H, d, J = 9.0 Hz, H6); ir: 1690 cm^{-1} (C=O str); ms: M Calcd. Found: M$^+$ = 212, 197 (M$^+$ -CH_3).

Anal. Calcd. for $C_{10}H_{12}OS_2$: C, 56.60; H, 5.66; S, 30.19. Found: C, 56.96; H, 5.83; S, 29.98.

Preparation of Oximes.

General Procedure.

The appropriate ketones **7c**, **8c**, **9c**, **10d**, **11b** or **14e** (approximately 5 mmoles) in methanol (10 ml) and pyridine (4 ml), with hydroxylamine hydrochloride (10 mmoles for **7c**, **8c**, **9c** and 5 mmoles for **10d**, **11b** and **14e**) were heated under reflux for 4 hours then poured into dilute ice cold hydrochloric acid and the precipitates collected. These were used without further purification for the next stage. Yields were approximately 90-95%.

Preparation of 7-Acetyl-3-methyl-6-methylthio-1,2-benzisothiazole (**11b**).

To a stirred solution of 3-methyl-6-methylthio-1,2-benzisothiazole (**11a**) (0.30 g, 1.7 mmoles) in dichloromethane (5 ml) and acetyl chloride (0.14 g, 1.7 mmoles) was added portionwise anhydrous aluminum chloride (0.5 g, 3.5 mmoles). The mixture was stirred 4 days then poured into ice water. Work up gave a yellow paste which was purified by column chromatography on silica gel using 25% ethyl acetate in cyclohexane as an eluent. The compound **11b** was crystallized from benzene as yellow needles, mp 142-143°, (40%); ^{1}H nmr: δ = 2.42 (2H, s, S-methyls), 2.53, 2.58 (two 3H, s, 3-methyl and acetyls), 7.45 (1H, d, J = 9 Hz, H5), 7.76 (1H, d, J = 9 Hz, H4); ir: 1640 cm^{-1} (C=O str); ms: M Calcd. = 237. Found: M$^+$ = 237, 222 (M$^+$ -CH_3). The exact mass Calcd. for $C_{11}H_{11}NOS_2$, 237.0282. Found: 237.0281.

Anal. Calcd. for $C_{11}H_{11}NOS_2$: C, 55.70; H, 4.64; N, 5.91; S, 27.00. Found: C, 55.88; H, 4.23; N, 6.06; S, 27.09.

2,5-Bis(methylthio)benzoic Acid (**14d**).

2-(Methylthio)benzoic acid (**14a**) (36 g, 0.2 mole) was added with stirring to chlorosulfonic acid (90 ml), while keeping the temperature below 20°. The mixture was stirred 24 hours then poured over ice and collected. The crude sulfonyl chloride **14d** obtained was dissolved in tetrahydrofuran (50 ml) and added to a stirred mixture of zinc powder (20 g), (amalgamated with mercuric chloride (2 g)) and concentrated hydrochloric acid (100 ml). After 4 hours the yellow precipitate which had formed was collected and extracted with ethyl acetate. The extract was filtered to remove zinc salts and evaporated to give the crude acid **14c**.

This was dissolved in 20% sodium hydroxide solution and treated with dimethyl sulfate (10 ml) with stirring. After 1 hour the solution was acidified with concentrated hydrochloric acid and the precipitate collected. It was recrystallized from benzene as pale yellow plates, mp 186-188°, (31%); ^{1}H nmr: δ = 2.43, 2.55 (two 3H, s, methyls), 7.13-7.63 (2H, m, H3, H4), 8.15 (1H, d, H6 proton); ir: 1688 cm^{-1} (C=O str); ms: M Calcd. = 214. Found: M$^+$ = 214, 199 (M$^+$ -CH_3).

Anal. Calcd. for $C_9H_{10}O_2S_2$: C, 50.47; H, 4.67; S, 29.91. Found: C, 50.43; H, 4.76; S, 29.68.

2,5-(Bismethylthio)acetophenone (**14e**).

2,5-(Bismethylthio)benzoic acid (**14d**) (2.14 g, 0.01 mole) in benzene (20 ml) with thionyl chloride (5 ml) was heated under reflux for 6 hours then the mixture was evaporated under reduced pressure. The acid chloride was dissolved in benzene and added to a one-fold excess of diethyl ethoxymagnesiummalonate prepared as above, and let stand 16 hours. The mixture was worked up as above, for **6c** giving a yellow oil, (86%). This was not further purified; ^{1}H nmr: δ = 2.33, 2.56 (two 3H, s, S-methyls), 2.55 (3H, s, acetyls), 7.18 (2H, m, H2, H3), 7.58 (1H, d, H6); ir: 1673 cm^{-1} (C=O str); ms: M Calcd. = 212. Found: M$^+$ = 212, 197 (M$^+$ -CH_3).

Preparation of 1,2-Benzisothiazoles **1b**, **3b**, **4b**, **5b**, **11a** and **12**.

General Procedure.

The appropriate oximes of 2-alkylthioarylketones *i.e.* **6e**, **7e**, **8e**, **11b**, **10e** or **14e**, respectively (approximately 1 g) in acetic anhydride (3 ml) and pyridine (15 ml) were heated under gentle reflux for 24 hours. The reaction mixtures were poured over ice cold dilute hydrochloric acid and extracted with chloroform. The chloroform layer was washed with 10% hydrochloric acid, 10% sodium hydroxide solution, dried and evaporated under reduced pressure. The products were purified by chromatography.

For **1b**, the benzodiisothiazole was obtained as yellow needles, mp 246-248°, (84%); ^{1}H nmr: δ = 2.86 (6H, s, methyls), 8.32 (1H, s, H8), 8.44 (1H, s, H4); ms: M Calcd. = 230. Found: M$^+$ = 220.

Anal. Calcd. for $C_{10}H_8N_2S_2$: C, 54.55; H, 3.64; N, 12.73; S, 29.09. Found: C, 54.15; H, 3.74; N, 12.63; S, 28.88.

For **3b**, the benzodiisothiazole was obtained as pale buff needles, mp 233-235°, (65%); ^{1}H nmr: δ = 2.85 (6H, s, methyls), 8.44 (2H, s, H4 and H8); ms: M Calcd. = 220. Found: M$^+$ = 220.

Anal. Calcd. for $C_{10}H_8N_2S_2$: C, 54.55; H, 3.64; N, 12.73; S, 29.09. Found: C, 54.25; H, 3.82; N, 12.63; S, 29.22.

For **4b**, the benzodiisothiazole was obtained as colorless prisms, mp 182-183° (24%); ^{1}H nmr: δ = 2.86 (6H, s, methyls), 7.89 (2H, s, H4 and H5); ms: M Calcd. = 220. Found: M$^+$ = 220.

Anal. Calcd. for $C_{10}H_8N_2S_2$: C, 54.55; H, 3.64; N, 12.73; S, 29.09. Found: C, 54.46; H, 3.71; N, 12.57; S, 29.39.

For **5b**, the benzodiisothiazole was obtained as yellow prisms, mp 142-143° (80%); ^{1}H nmr: δ = 2.85 (3H, s, 8-methyls), 2.94 (3H, s, 3-methyls), 7.90 (1H, d, J = 9.0 Hz, H5), 7.97 (1H, d, J = 9.0 Hz, H4); ms: M Calcd. = 220. Found: M$^+$ = 220.

Anal. Calcd. for $C_{10}H_8N_2S_2$: C, 54.55; H, 3.64; N, 12.73; S, 29.09. Found: C, 54.36; H, 3.70; N, 12.69; S, 28.93.

For **11a**, the benzisothiazole was obtained as buff prisms, mp 58-60°, (92%); ^{1}H nmr: δ = 2.50 (3H, S-methyls), 2.63 (3H, s, 3-methyls), 7.16 (1H, d, J = 7.8 Hz, H5), 7.56 (1H, s, H7), 7.63 (1H, d, J = 7.8 Hz, H4); ms: M Calcd. = 195. Found: M$^+$ = 195, 180 (M$^+$ -CH_3).

Anal. Calcd. for $C_9H_9NS_2$: C, 55.38; H, 4.61; N, 7.18; S, 32.82. Found: C, 55.07; H, 4.65; N, 7.23; S, 32.88.

For **12**, the benzisothiazole was obtained as buff prisms, mp 65°, (89%); ^{1}H nmr: δ = 2.54 (3H, s, S-methyls), 2.66 (3H, s, 3-methyls), 7.40 (1H, d, J = 7.8 Hz, H7), 7.73 (1H, s, H4), 7.80 (1H, d, J = 7.8 Hz, H6); ms: M Calcd. = 195. Found: M$^+$ = 195, 180 (M$^+$ -CH_3).

Attempted Acetylation of 3-Methyl-5-methylthio-1,2-benzisothiazole (**12**).

This compound was treated with acetyl chloride and aluminum chloride as for the compound **11b**. Work up afforded starting material.

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