Heterofulvalenes. II. Synthesis and Reaction of 2,3 : 7,8-Dibenzo-1,4-dithia-6-azafulvalene

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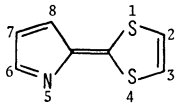
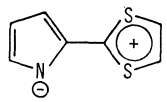
Reaction of 2-isopentyloxy-1,3-benzodithiole with indole in acetic acid gave a 93% yield of 3-(1,3-benzodithiol-2-yl)indole (**4a**) which was converted to 2-(3-indolyl)-1,3-benzodithiolylium tetrafluoroborate (**5a**) in a 77% yield by treatment with trityl tetrafluoroborate. **5a** was also prepared by reaction of indole with 2 molar amounts of 1,3-benzodithiolylium tetrafluoroborate. Treatment of **5a** with triethylamine afforded the title compound **6a** in 93% yield. **6a** was protonated, methylated, and benzoylated at its 6-position by tetrafluoroboric acid, methyl iodide, and benzoyl chloride, respectively. Reaction of **6a** with dimethyl acetylenedicarboxylate gave a 1,6-dipolar intermediate which was trapped as an adduct with ethanol. **6a** was smoothly reduced by sodium borohydride to give its 5,6-dihydro derivative.

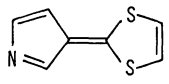
In recent years synthetic studies of tetrathia- and tetraselenafulvalenes and their derivatives have been extensively done in order to find excellent organic semiconductors.[1] In this connection, 1,4-dithia-azafulvalenes seem to be compounds of current interest, although only slight attention has been paid to their chemistry.[2] In Part I of this series, we reported the synthesis of 1,4-dithia-5-aza- and 6-azafulvalenes (**1** and **2**), and their spectroscopic properties are suggestive of the considerable contribution of the polarlized structures (**1′** and **2′**) to the ground state of these compounds.[3] We now report the synthetic studies of dibenzo analogs of **1** and **2** and the reaction of the title compound.



1



1′



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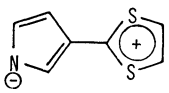
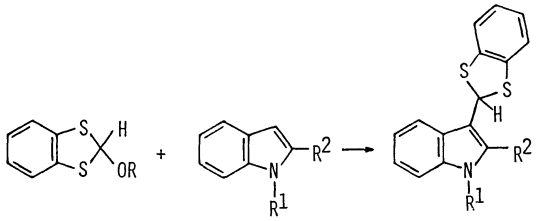


2′

Results and Discussion

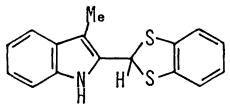
Synthesis. 2-Isopentyloxy-1,3-benzodithiole (**3**) which has recently become readily obtainable[4] can react with a wide variety of nucleophiles.[5] Thus, **3** reacted with indole at room temperature to give 3-(1,3-benzodithiol-2-yl)indole (**4a**) in a 93% yield. Similarly, **3** reacted with 2-methyl- and 1-methylindoles giving **4b** (98%) and **4c** (95%), respectively. 3-Methylindole, carrying a methyl at its most reactive position towards electrophiles, reacted at its 2-position to give **4d** in a 96% yield.[6]

In the light of the reaction of 1,3-benzodithiole with trityl tetrafluoroborate (**7**) producing 1,3-benzodithiolylium tetrafluoroborate (**8**) in a good yield,[8] treatment of **4a** with **7** seems to be a promising route to 2-(3-indolyl)-1,3-benzodithiolylium tetrafluoroborate (**5a**). Thus, **4a** smoothly reacted with an equivalent of **7** to give the desired product **5a** in a 77% yield. Similarly,



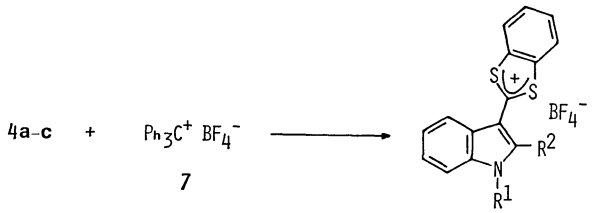
3
(R = $CH_2CH_2CHMe_2$)

4a : $R^1 = R^2 = H$
4b : $R^1 = H$, $R^2 = Me$
4c : $R^1 = Me$, $R^2 = H$



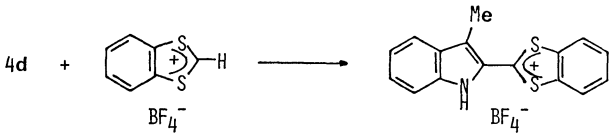
4d

treatment of **4b** and **4c** with **7** gave **5b** (75%) and **5c** (71%), respectively. However, the reaction of **4d** with **7** failed to furnish **5d** (a 68% yield of **4d** was recovered



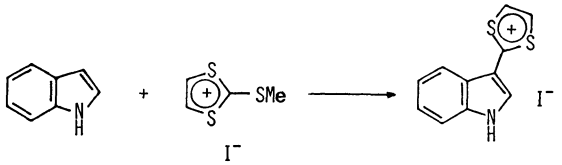
7

5a : $R^1 = R^2 = H$
5b : $R^1 = H$, $R^2 = Me$
5c : $R^1 = Me$, $R^2 = H$



8

5d



9

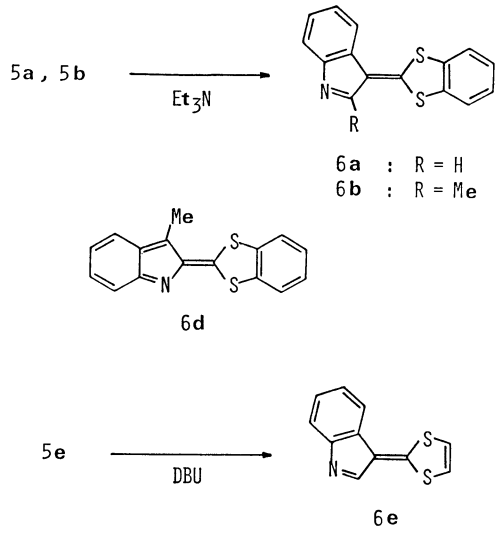
5e

and the yield of triphenylmethane resulting from hydride abstraction by trityl cation was only 15%).

Recent studies have shown that **8** can abstract a hydride from 2-substituted 1,3-benzodithioles yielding 2-substituted 1,3-benzodithiolylium tetrafluoroborates.[3,9] In fact, treating **4d** with an equivalent of **8** afforded **5d** in a 63% yield. This result, together with the fact that the formation of **4** from **3** and indoles involves 1,3-benzodithiolylium ion as intermediate,[7] is indicative that treatment of indoles with 2 molar amounts of **8** would produce **5** in a single step; one mole of **8** reacts with indoles to give **4** and another mole of **8** abstracts a hydride from **4** to yield **5**. Expectedly, the reaction of 3-methylindole with 2 molar amounts of **8** furnished **5d** in a 54% yield. In a similar way, **5a** (60%) and **5b** (51%) were also obtained.

We also prepared 2-(3-indolyl)-1,3-dithiolylium iodide (**5e**); heating indole with the salt **9** at 50 °C in acetonitrile gave **5e** in a 58% yield. However, **9** failed to react with 3-methylindole.

The final step is the deprotonation of **5**. In the case of **5a** and **5b**, this was easily achieved by treating them with triethylamine in acetonitrile at 0 °C; the title compound **6a** and its methyl derivative **6b** were obtained in 93 and 92% yields, respectively. However, treatment of an acetonitrile solution of **5d** with triethylamine resulted in the black reaction mixture, from which an unstable compound, which was converted to the starting material **5d** on treatment with tetrafluoroboric acid, was isolated in a good yield. We could not detect the presence of the desired product **6d**. Attempted trapping of **6d** by dimethyl acetylenedicarboxylate was also unsuccessful. Treatment of **5e** with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as base yielded **6e** quantitatively.



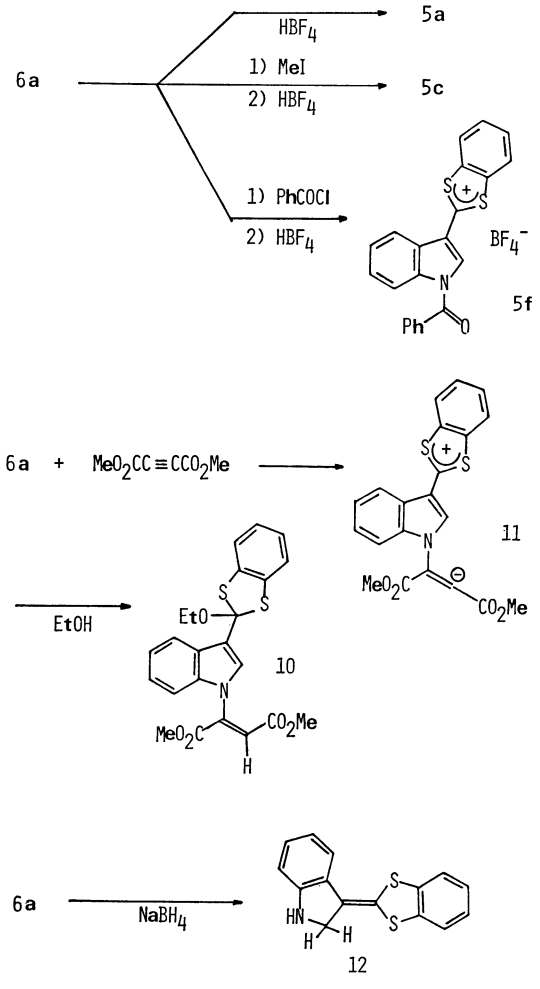
Reaction. Broadly speaking, the spectroscopic features of compounds **5** and **6** are similar to those observed with **1**, **2**, and their protonated species[3] (see Experimental section).

Treatment of **6a** with tetrafluoroboric acid gave **5a** quantitatively. Heating **6a** with methyl iodide and then treating the resulting product with tetrafluoroboric acid gave **5c** in a 91% overall yield. When **6a** was allowed to react with benzoyl chloride in acetonitrile and then the mixture was treated with tetrafluoroboric acid, a 70% yield of 2-(1-benzoyl-3-indolyl)-1,3-benzodithiolylium tetrafluoroborate (**5f**) was obtained.

Heating **6a** with dimethyl acetylenedicarboxylate in boiling chloroform containing ethanol produced compound **10** in a 60% yield. The IR spectrum of **10** has absorptions at 1735 and 1705 cm^{-1} due to the ester carbonyl groups. The NMR spectrum determined in $CDCl_3$ showed two singlets of methyls at 3.80 and 3.96 ppm, a triplet of methyl at 1.26 ppm, and a quartet of methylene at 3.67 ppm. The *trans* geometry of the methoxycarbonyl groups was elucidated from the chemical shift value of the olefinic proton which appeared at 6.27 ppm. It is documented that the olefinic proton of the *trans* form of this type of compounds appears at 5.99—6.27 ppm, whereas that of the *cis* form resonates at 6.63—6.94 ppm.[10] The formation of **10** can best be rationalized by capture of the 1,6-dipolar intermediate **11** by ethanol.

In all the examples described above, **6a** easily reacted at its 6-position with electrophiles. This can be understood as a result of the contribution of polarlized structure corresponding to **2'** to the ground state of **6a**.

Reaction of **6a** with nucleophiles was next examined. **6a** resisted reaction with phenylmagnesium bromide, but it smoothly reacted with sodium borohydride at



room temperature in a mixture of tetrahydrofuran and water. Workup of the mixture gave **12**, the dihydro derivative of **6a**, in an 89% yield as unstable compound in solution. Structure of **12** was determined by spectroscopic and elemental analyses. The result indicates that hydride ion as nucleophile attacks on the 5-position of **6a** rather than the dithiole ring carbon. This is not in harmony with the expected reactivity of **6a** from the contribution of the canonical structure like **2'** and further investigation, emphasis placed on this point, will be needed.

Experimental

2-Isopentoxy-1,3-benzodithiole (**3**),[4] trityl[11] and 1,3-benzodithiolylium[8] tetrafluoroborates (**7** and **8**), and 2-methylthio-1,3-dithiolylium iodide (**9**)[12] were prepared by reported methods. Acetonitrile was refluxed over and distilled from calcium hydride.

Preparation of 4. 3-(1,3-Benzodithiol-2-yl)indole (**4a**). A solution of 1.17 g (10 mmol) of indole and 2.64 g (11 mmol) of **3** in 30 ml of acetic acid was allowed to stand at room temperature for 4 h. The solution was diluted with 100 ml of water, and the resulting precipitate was triturated, collected, washed with water, and dried to give 2.50 g (93%) of **4a**, which melted at 96—98 °C after recrystallization from cyclohexane. NMR ($CDCl_3$) δ 6.60 (1H, s, methine), 6.9—7.4 (8H, m), and 7.7—7.9 (2H, m). Found: C, 66.95; H, 4.19; N, 5.18; S, 23.78%. Calcd for $C_{15}H_{11}NS_2$: C, 66.91; H, 4.12; N, 5.20; S, 23.77%.

In a similar way as described with **4a**, compounds **4b—d** were prepared in 98, 95, and 96% yields, respectively.

3-(1,3-Benzodithiol-2-yl)-2-methylindole (**4b**), mp 120—121 °C (from ethanol). NMR ($CDCl_3$) δ 2.30 (3H, s, Me), 6.90 (1H, s, methine), 6.95—7.30 (7H, m), 7.65 (1H, broad s, NH), and 7.95 (1H, m). Found: C, 67.30; H, 4.65; N, 4.95; S, 22.70%. Calcd for $C_{16}H_{13}NS_2$: C, 67.84; H, 4.63; N, 4.95; S, 22.59%.

3-(1,3-Benzodithiol-2-yl)-1-methylindole (**4c**), mp 139—140 °C. NMR ($CDCl_3$) δ 3.60 (3H, s, Me), 6.58 (1H, s, methine), 6.8—7.3 (8H, m), and 7.7 (1H, m). Found: C, 67.70; H, 4.66; N, 5.01; S, 22.57%. Calcd for $C_{16}H_{13}NS_2$: C, 67.84; H, 4.63; N, 4.95; S, 22.59%.

2-(1,3-Benzodithiol-2-yl)-3-methylindole (**4d**), mp 127—128 °C (from cyclohexane). NMR ($CDCl_3$) δ 2.26 (3H, s, Me), 6.64 (1H, s, methine), 7.0—7.3 (7H, m), 7.45—7.55 (1H, m), and 8.3 (1H, broad s, NH). Found: C, 67.96; H, 4.68; N, 4.89; S, 22.45%. Calcd for $C_{16}H_{13}NS_2$: C, 67.84; H, 4.63; N, 4.95; S, 22.59%.

2-(3-Indolyl)-1,3-benzodithiolylium Tetrafluoroborate (5a).

a) From 4a and 7: A solution of 2.59 g (7.85 mmol) of **7** in 15 ml of anhydrous acetonitrile was added dropwise over a period of 15 min to a stirred and ice-cooled solution of 2.11 g (7.85 mmol) of **4a** in 15 ml of anhydrous acetonitrile. The mixture was warmed to room temperature and stirred for 1 h. The resulting crystalline precipitate was collected and washed with a small amount of acetonitrile to give 2.17 g (77%) of **5a**, which melted at 246—247 °C (dec) (orange needles) after recrystallization from acetonitrile. IR (Nujol) 3300 (NH) and 1000—1120 cm^{-1} (BF_4^-); NMR (CF_3CO_2D, 65 °C), δ 7.5—7.7 (3H, m), 7.7—8.2 (4H, AA'XX'm), 8.02 (1H, m), and 8.70 (1H, s, -NH-C<u>H</u>=); UV (CH_3CN) (log ε) 453 nm (4.69). Found: C, 50.57; H, 2.85; N, 3.85%. Calcd for $C_{15}H_{10}NS_2BF_4$: C, 50.72; H, 2.84; N, 3.94%.

b) From Indole and 2 Molar Amounts of 8: A soliuton of 2.40 g (10 mmol) of **8** in 15 ml of anhydrous acetonitrile was added dropwise during 10 min to a stirred and ice-cooled solution of 0.59 g (5 mmol) of indole in 5 ml of anhydrous acetonitrile. After stirring for 4 h at room temperature, the resulting crystalline precipitate was collected and washed with a small amount of acetonitrile to give 0.85 g of **5a** as orange crystals. The filtrate was diluted with 10 ml of ether and the resulting precipitate was collected to give another crop of **5a** (0.23 g); total yield (60%). **5a**, thus obtained, agreed in all respects with a specimen obtained from **4a** and **7**.

2-(2-Methyl-3-indolyl)-1,3-benzodithiolylium Tetrafluoroborate (5b). Under the same conditions as described with **5a**, 1.42 g (5 mmol) of **4b** and 1.65 g (5 mmol) of **7** gave 1.38 g (75%) of **5b**, mp 284—286 °C (dec), yellow needles (from acetonitrile). IR (Nujol) 3270 (NH) and 1000—1120 cm^{-1} (BF_4^-); NMR (CF_3CO_2D) δ 2.93 (3H, s, Me), 7.4—7.6 (3H, m), 7.7—8.2 (4H, AA'XX'm), and *ca.* 8.0 (1H, m); UV (CH_3CN) (log ε) 441 nm (4.57). Found: C, 52.04; H, 3.33; N, 3.63%. Calcd for $C_{16}H_{12}NS_2BF_4$: C, 52.05; H, 3.28; N, 3.79%.

5b was also obtained from 2-methylindole and 2 molar amounts of **8** in a 51% yield.

2-(1-Methyl-3-indolyl)-1,3-benzodithiolylium Tetrafluoroborate (5c). Under the same conditions as described with **5a**, 1.42 g (5 mmol) of **4c** and 1.65 g (5 mmol) of **7** gave 1.32 g (71%) of **5c**, mp 276—278 °C, orange needles (from acetonitrile). NMR (CF_3CO_2D) δ 4.02 (3H, s, Me), 7.5—8.2 (8H, m), and 8.62 (1H, s, -NMe-C<u>H</u>=). Found: C, 52.17; H, 3.25; N, 3.63%. Calcd for $C_{16}H_{12}NS_2BF_4$: C, 52.05; H, 3.28; N, 3.79%.

2-(3-Methyl-2-indolyl)-1,3-benzodithiolylium Tetrafluoroborate (5d). *a) From 4d and an Equivalent of 8*: A solution of 576 mg (2.4 mmol) of **8** in 4 ml of anhydrous acetonitrile was added dropwise over a period of 10 min to a stirred and ice-cooled solution of 680 mg (2.4 mmol) of **4d** in 10 ml of acetonitrile. The mixture was stirred for 3 h while warmed to room temperature. The resulting precipitate was collected to give 557 mg (63%) of **5d**, mp 236—237 °C (dec), violet needles (from acetonitrile). NMR (CF_3CO_2D) δ 2.74 (3H, s, Me), 7.13 (1H, m), 7.45 (2H, m), 7.69 (1H, d), and 7.76—8.30 (4H, m, AA'XX'm); UV (CH_3CN) (log ε) 467 nm (4.70). Found: C, 52.21; H, 3.40; N, 3.52; S, 17.33%. Calcd for $C_{16}H_{12}NS_2BF_4$: C, 52.05; H, 3.28; N, 3.79; S, 17.37%.

b) From 3-Methylindole and 2 Molar Amounts of 8: Under the same conditions as described with **5a**, 1.31 g (10 mmol) of 3-methylindole and 5.28 g (22 mmol) of **8** gave 1.98 g (54%) of **5d**, mp 231—233 °C (dec).

c) Attempted Synthesis from 4d and 7: A solution of 0.83 g (2.5 mmol) of **7** in 10 ml of anhydrous acetonitrile was added dropwise over a period of 10 min to a stirred and ice-cooled solution of 0.71 g (2.5 mmol) of **4d** in 20 ml of anhydrous acetonitrile. After stirring for 2 h, the mixture turned dark red without precipitation of product. Dilution of the mixture with 30 ml of anhydrous ether also caused no precipitation. Therefore, the mixture was poured into 100 ml of ice water and extracted with three 100 ml portions of ether. The extract was washed with water, dried, and evaporated. The residure was chromatographed on a column of silica gel, which afforded 0.10 g (15%) of triphenylmethane, mp 93—94 °C, 0.47 g (68%) of **4d**, and 0.36 g (53%) of triphenylmethanol, mp 161—162 °C.

2-(3-Indolyl)-1,3-dithiolylium Iodide (5e). A mixture of 117 mg (1 mmol) of indole and 276 mg (1 mmol) of **9** in 15 ml of anhydrous acetonitrile was heated at 50 °C for 8 h. The resulting crystalline precipitate was collected to give 200 mg

(58%) of **5e**, mp 280 °C, reddish brown needles (from DMF–nitromethane). UV (CH_3CN) (log ε) 438 nm (3.53); NMR (DMSO-d_6) δ 7.3—8.2 (4H, m), 8.50 (2H, s, dithiole ring), and 9.07 (1H, s, –NH–CH=). Found: C, 38.30; H, 2.29; N, 4.01; S, 18.75%. Calcd for $C_{11}H_8INS_2$: C, 38.27; H, 2.34; N, 4.06; S, 18.57%.

2,3 : 7,8-Dibenzo-1,4-dithia-6-azafulvalene (6a). To a stirred and ice-cooled solution of 0.71 g (2 mmol) of **5a** in 20 ml of anhydrous acetonitrile was added dropwise 0.5 ml of triethylamine. The reaction occurred immediately with precipitation of yellow crystals. After stirring for 1 h at room temperature, the precipitate was collected and washed with acetonitrile to give 0.50 g (93%) of **6a**, which melted at 212—213 °C (yellow needles) after recrystallization from benzene. IR (Nujol) 1600, 1578, 1566, 1538, 1460, 1438, 1290, 1220, 1195, 875, 765, and 740 cm^{-1}; UV (C_6H_6) (log ε) 417 nm (4.55); MS *m/e* 267 (M^+); NMR ($CDCl_3$) δ 7.2—7.4 (4H, m), 7.4—7.7 (4H, m), and 8.20 (1H, s, –N–CH=). Found: C, 67.76; H, 3.61; N, 5.24; S, 23.83%. Calcd for $C_{15}H_9NS_2$: C, 67.41; H, 3.39; N, 5.24; S, 23.95%.

5-Methyl-2,3: 7,8-dibenzo-1,4-dithia-6-azafulvalene (6b). Treatment of 0.74 g (2 mmol) of **5b** with 0.5 ml of triethylamine at 0 °C gave 0.52 g (92%) of **6b**, mp 183—184 °C (dec), yellow needles (from benzene). UV (C_6H_6) (log ε) 400 nm (4.40); MS *m/e* 281 (M^+); MNR ($CDCl_3$) δ 2.58 (3H, s, Me), 7.15—7.36 (4H, m), and 7.40—7.70 (4H, m). Found: C, 68.72; H, 4.02; N, 4.83; S, 22.67%. Calcd for $C_{16}H_{11}NS_2$: C, 68.32; H, 3.94; N, 4.98; S, 22.75%.

7,8-Benzo-1,4-dithia-6-azafulvalene (6e). To a stirred solution of 200 mg (0.58 mmol) of **5e** in 20 ml of anhydrous acetonitrile was added 0.1 ml of DBU. The mixture was stirred for 0.5 h and diluted with 100 ml of ice water. The resulting precipitate was collected, washed with water, and dried to give 108 mg (100%) of **6e** as golden yellow crystals, mp 134—135 °C. MS *m/e* (%) 217 (M^+, 100), 159 (8), 149 (32), 78 (22), and 76 (33); NMR ($CDCl_3$) 6.85 (2H, s, dithiole ring), 7.15—7.80 (4H, m, benzene ring), and 8.17 (1H, d, –N–C=H–). Found: C, 60.95; H, 3.31; N, 6.22%. Calcd for $C_{11}H_7NS_2$: C, 60.79; H, 3.25; N, 6.45%.

Attempted Synthesis of 6d. To a stirred and ice-cooled suspension of 369 mg (1 mmol) of **5d** in 13 ml of anhydrous acetonitrile was added 0.3 ml of triethylamine. The yellow suspension turned dark red immediately. The mixture was stirred for 1.5 h at room temperature and a small amount of tarry insoluble material was filtered off. The dark filtrate was diluted with water and the resulting precipitate was collected and washed with methanol to give 200 mg of a pink solid, mp 154—156 °C; IR (Nujol) 3380 (NH) and 1115 cm^{-1} (aliphatic ether). Attempted purification of this compound by recrystallization or reprecipitation suffered extensive decomposition. The addition of 1 ml of 42% tetrafluoroboric acid to a solution of 209 mg of this compound in 10 ml of acetic anhydride resulted in the formation of 154 mg of **5d**.

To a stirred and ice-cooled solution of 156 mg (1.1 mmol) of dimethyl acetylenedicarboxylate and 0.2 ml of triethylamine in 20 ml of anhydrous acetonitrile was added 369 mg (1 mmol) of **5d** in small portions. The mixture was warmed to room temperature and heated at 50 °C for 5 h. Workup of the mixture gave only intractable tars.

Treatment of 6a with Tetrafluoroboric Acid. A mixture of 67 mg (0.25 mmol) of **6a** in 2 ml of 42% tetrafluoroboric acid was stirred for 0.5 h and the resulting precipitate was collected and washed with anhydrous ether to give 87 mg (98%) of **5a**.

Treatment of 6a with Methyl Iodide. To a stirred suspension of 195 mg (0.73 mmol) of **6a** in 10 ml of acetonitrile was added 0.5 ml of methyl iodide and the mixture was heated under reflux for 1 h. The resulting precipitate was collected to give 278 mg (93%) of 2-(1-methyl-3-indolyl)-1,3-benzodithiolylium iodide as red crystals, whose IR spectrum is essentially the same as that of **6a**. This compound (123 mg) was stirred in a mixture of 1 ml of 42% tetrafluoroboric acid and 5 ml of acetic anhydride for 20 min to give 109 mg of **5c**, mp 275—277 °C, whose IR spectrum agreed in all respects with that of a specimen obtained from **4c** and **7**.

Tretment of 6a with Benzoyl Chloride. A mixture of 134 mg (0.5 mmol) of **6a** and 141 mg (1 mmol) of benzoyl chloride in 10 ml of acetonitrile was stirred at room temperature for 0.5 h. The mixture was cooled to 0 °C and a mixture of 1 ml of 42% tetrafluoroboric acid and 10 ml of acetic anhydride was added. After stirring for 1 h at room temperature, the resulting precipitate was collected and washed with ether to give 161 mg (70%) of 2-(1-benzoyl-3-indolyl)-1,3-benzodithiolylium tetrafluoroborate (**5f**), mp 240 °C, yellowish orange needles (from acetonitrile). IR (Nujol) 1700 (C=O) and 1000—1120 cm^{-1} (BF_4^-). Found: C, 57.32; H, 3.00; N, 2.83; S, 14.07%. Calcd for $C_{22}H_{14}NOS_2BF_4$: C, 57.53; H, 3.07; N, 3.05; S, 13.96%.

Reaction of 6a with Dimethyl Acetylenedicarboxylate. To a stirred solution of 267 mg (1 mmol) of **6a** in 15 ml of chloroform containing 0.5—0.9% of ethanol as a stabilizer was added a solution of 312 mg (2.2 mmol) of dimethyl acetylenedicarboxylate in 5 ml of chloroform. The mixture was stirred for 0.5 h at room temperature and then refluxed for 2 h. Analysis by TLC showed the formation of a single product. Evaporation of the solvent left a yellow solid, which was washed with ether to give 216 mg (60%) of **10**, mp 171.5—172 °C (from CCl_4), colorless needles. IR (Nujol) 1735 and 1705 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.26 (3H, t, J=7 Hz, Me), 3.67 (2H, q, J=7 Hz, CH_2), 3.80 (3H, s, Me), 3.96 (3H, s, Me), 6.27 (1H, s, olefinic), 7.1—7.6 (8H, m), and 7.9 (1H, m). Found: C, 60.42; H, 4.51; N, 3.13; S, 13.86%. Calcd for $C_{23}H_{21}NO_5S_2$: C, 60.66; H, 4.65; N, 3.08; S, 14.05%.

Reduction of 6a with Sodium Borohydride. To a stirred mixture of 80 mg (2.1 mmol) of sodium borohydride in 20: 1 tetrahydrofuran/water (21 ml) was added 267 mg (1 mmol) of **6a** in small portions. The mixture was stirred for 0.5 h and a trace amount of insoluble material was filtered off. The filtrate was diluted with 20 ml of water and the resulting precipitate was collected and dried to give 240 mg (89%) of **12** as faint yellow crystals, mp 128—129 °C. This compound is unstable in solution; when it was dissolved in chloroform, yellow polymeric material, scarcely soluble in organic solvents, deposited a few minutes later. This made it impossible to obtain a good NMR spectrum; δ ($CDCl_3$) 4.10 (2H, s, CH_2) and 6.5—7.4 (8 or 9H, m). IR (KBr) 3380 (NH), 3050, 2870, and 2840 (CH_2), 1605, 1585, 1475, 1445, 1320, 1280, 1250, and 740 cm^{-1}. Found: C, 66.64; H, 4.17; N, 5.44; S, 23.71%. Calcd for $C_{15}H_{11}NS_2$: C, 66.91; H, 4.12; N, 5.20; S, 23.77%.

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