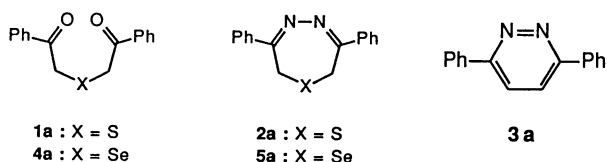


Preparation of 3,6-Disubstituted Pyridazines from 3-Thiapentane-1,5-diones via 2,7-Dihydro-1,4,5-thiadiazepines

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A series of 3-thiapentane-1,5-diones condense with hydrazine in the presence of a catalytic amount of *p*-toluenesulfonic acid in refluxing ethanol to give 2,7-dihydro-1,4,5-thiadiazepines in excellent yields. Thermal decomposition of the latter compounds in refluxing diethylene glycol affords the corresponding pyridazines in high yields with evolution of hydrogen sulfide. The above procedure is generally applicable to the preparation of a wide variety of 3,6-disubstituted pyridazines which are of structural interest and otherwise difficult to prepare.

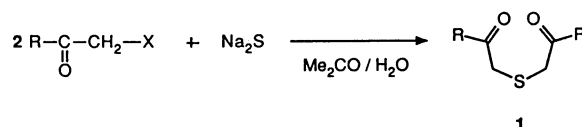
In recent years we have been investigating the synthesis using 3-thia- and 3-selenapentane-1,5-diones as the starting materials.^{1,2)} In this connection, we were interested in the reports by Loudon and Young³⁾ and by Ajello.⁴⁾ The former group reports that the thermolysis of 2,7-dihydro-3,6-diphenyl-1,4,5-thiadiazepine (**2a**), obtainable by condensation of 1,5-diphenyl-3-thiapentane-1,5-dione (**1a**) with hydrazine, affords 3,6-diphenylpyridazine (**3a**) with evolution of hydrogen sulfide. The latter author also describes the formation of **3a** by thermolysis of 2,7-dihydro-3,6-diphenyl-1,4,5-selenadiazepine (**5a**) obtainable from 1,5-diphenyl-3-selenapentane-1,5-dione (**4a**). These reactions apparently seem to provide promising routes to substituted pyridazines. Their synthetic utility, however, has not been fully explored. We therefore planned to establish the generality of the above synthesis. We have chosen 3-thiapentane-1,5-diones (**1**) as the starting material since a wide variety of **1** are readily obtainable. Although 3-selenapentane-1,5-diones had become readily obtainable,^{2a)} the use of these compounds was abandoned because thermolysis of 2,7-dihydro-1,4,5-selenadiazepines might evolve highly toxic hydrogen selenide. Thus, herein we report the general synthesis of 3,6-disubstituted pyridazines (**3**) from **1** via 2,7-dihydro-1,4,5-thiadiazepines (**2**).



Results and Discussion

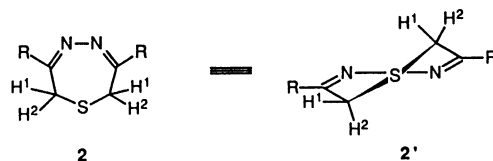
3-Thiapentane-1,5-diones (**1**) are easily prepared in good yields by adding an aqueous solution of sodium sulfide to a stirred and ice-cooled solution of an α -halo ketone in acetone.⁵⁾ Some α -halo ketones are commercial sources and were used as purchased and the others were prepared by bromination of the corresponding methyl ketones.⁶⁾ The yields of **1** thus

obtained are summarized in the Scheme 1.

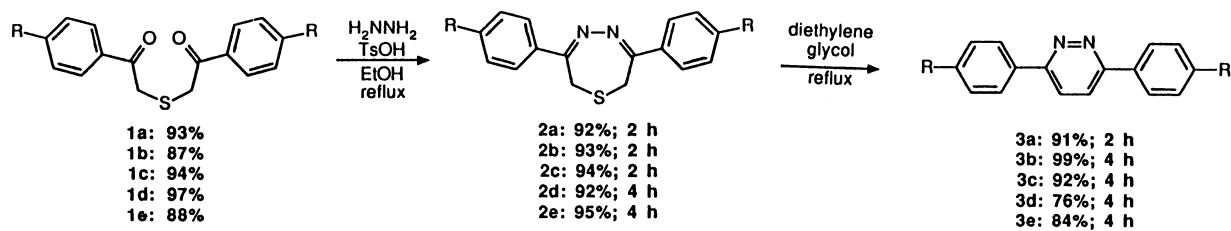


2,7-Dihydro-1,4,5-thiadiazepines (**2**) were obtained by condensation of **1** with hydrazine. The best results are generally attained by heating **1** with 1.6 equiv of hydrazine monohydrate in refluxing ethanol in the presence of a catalytic amount of *p*-toluenesulfonic acid (TsOH). Only **2g** was prepared by condensation in hot acetic acid. Reaction conditions and the yields of **2** are also summarized in the Scheme 1.

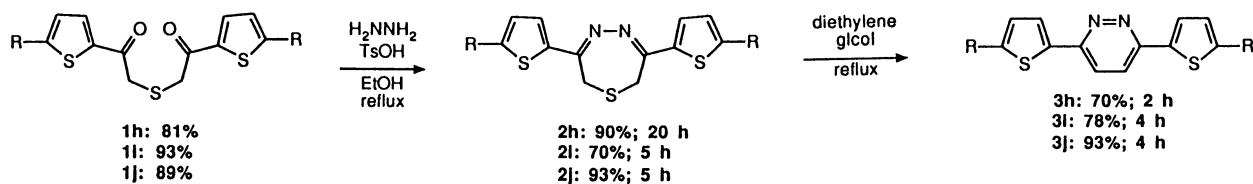
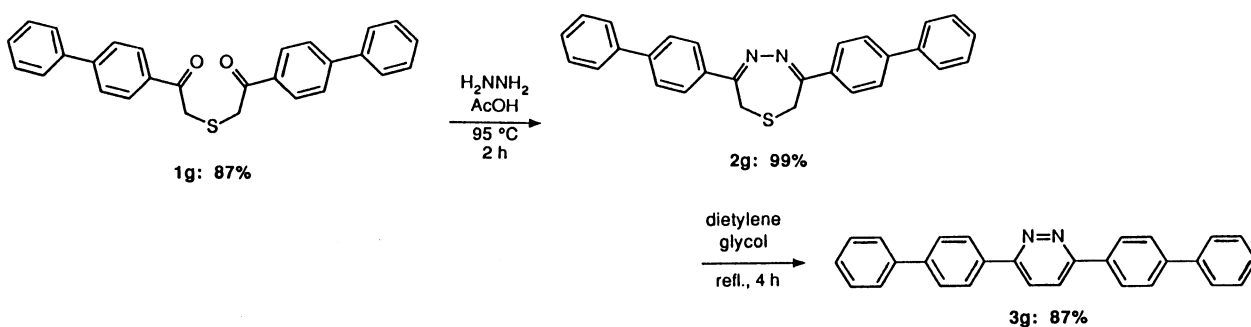
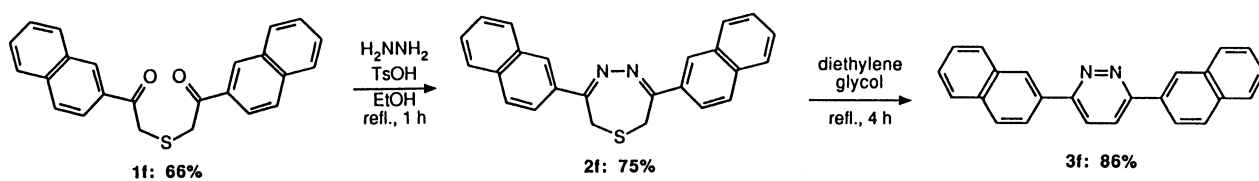
Sataty has shown that some 2,7-dihydro-1,4,5-thiadiazepines exist in a skew-boat conformation in solutions.⁷⁾ Actually, in the ¹H NMR spectra determined in deuterochloroform as the solvent at 27°C, the methylene protons of every **2** appear as AB quartet with $J=12$ – 13 Hz. These observations show that all of **2** exist in the skew-boat conformation **2'**, which results in the chemical shift non-equivalence of the methylene protons H¹ and H², in solutions around room temperature. The doublets of compounds **2h**–**j** appear as rather broad signals. This suggests that the ring inversion of these compounds occurs to some extent, while that of the other compounds are slow enough on the ¹H NMR time scale at room temperature.



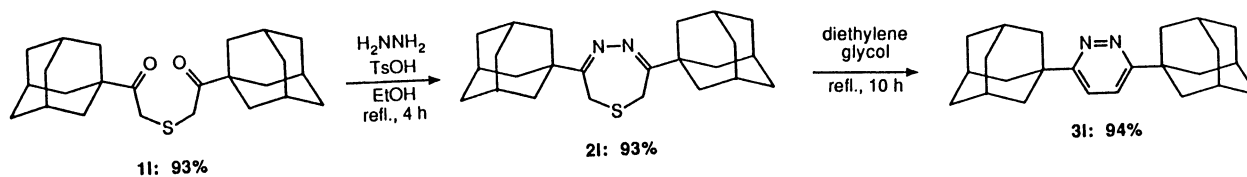
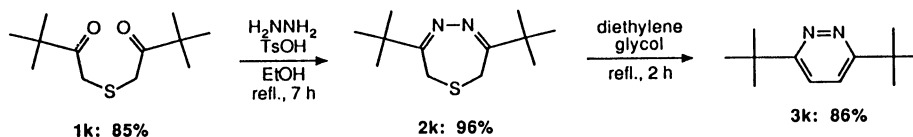
Conversion of **2** to the corresponding 3,6-disubstituted pyridazines **3** was cleanly attained by heating **2** in refluxing diethylene glycol. The evolution of hydrogen sulfide was observed in every case during the reaction. Reaction conditions and the yields of **3**



a: R=H, b: R=Me, c: R=OMe, d: R=Cl, e: R=Br



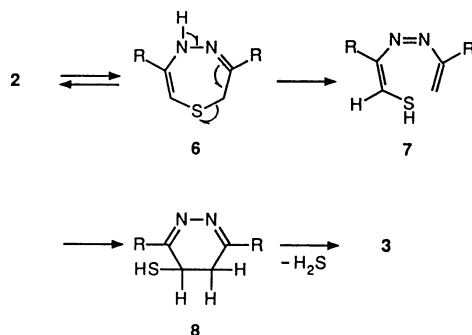
h: R=H, i: R=Cl, j: R=Br



Scheme 1.

thus prepared are summarized in the Scheme 1.

As to the mechanism of the above thermolysis, the followings seem plausible. When **2** were heated in a highly polar solvent diethylene glycol, they probably partly tautomerize to the amino forms **6**, although we could not obtain the evidence for the existence of **6** by ^1H NMR and IR spectra determined in deuteriochloroform and carbon tetrachloride, respectively, at room temperature. Then **6** should undergo the carbon (sp^3)-sulfur bond cleavage to lead to the heterotrienes **7**, which in turn undergo electrocyclic ring closure to afford the heterocycles **8**. Finally **8** aromatize to give the final products **3** with loss of hydrogen sulfide.⁸⁾



The synthetic method of **3** described above is convenient from the following points of view.

a) The standard method of synthesis of the pyridazine ring involves the action of hydrazine on 1,4-dicarbonyl compounds or their equivalent.⁹⁾ The preparation of 1,4-dicarbonyl compounds, however, often requires tedious or sophisticated procedures. In the present case, the starting **1** are readily obtainable.

b) None of the steps in the present synthesis requires any expensive reagents or special techniques. Work-up procedure is also simple and good overall yields are attained.

c) The method provides the synthesis of pyridazines which are of interest as the starting compounds for the preparation of conducting materials (**3g–j**).

d) The method allows the preparation of pyridazines having highly bulky groups such as *t*-butyl and 1-adamantyl (**3k** and **3l**).

Experimental

General. Melting points were determined on a MEL-TEMP capillary tube apparatus and are uncorrected. ^1H NMR spectra were recorded on a JEOL PMX-60, a JEOL FX-90Q, or a Bruker AM-400 spectrometer and ^{13}C NMR spectra on a JEOL FX-90Q or on a Bruker AM-400 spectrometer. Chemical shifts are expressed in parts per million from tetramethylsilane as an internal standard. Mass spectra were measured on a Shimadzu QP-1000 spectrometer with ionization energy of 70 or 20 eV. High resolution mass spectra were determined on a JEOL DX-303 spectrometer. IR spectra were taken on a Hitachi 270-50

spectrometer. UV spectra were recorded on a Hitachi 340 spectrometer. Column chromatography was conducted using E. Merck silica gel 60 (70–230 mesh). Sodium sulfide enneahydrate, hydrazine monohydrate, and diethylene glycol are commercial sources and were used as purchased.

Elemental analyses were performed by Analytical Center of Saitama University, for which we thank Professor M. Sato and his staff.

General Procedure for the Preparation of 3-Thiapentane-1,5-diones (1). A solution of sodium sulfide enneahydrate (5 mmol) in 10 ml of water was added to a stirred and ice-cooled solution of an α -halo ketone (10 mmol) in an appropriate amount of acetone (20–60 ml). After completion of the addition, the mixture was warmed to room temperature and stirred for a few hours. The resulting crystalline precipitate was collected by filtration, washed with water and then with a small amount of cold methanol or ethanol, and recrystallized from an appropriate solvent. In the case of the crystalline precipitate being not separated or separated only in a small amount, the mixture was concentrated and the resulting precipitate was treated as described above.

2-Bromo-, 2-bromo-4'-methyl-, 2-bromo-4'-methoxy-, 2-bromo-4'-chloro-, 2,4'-dibromo-, and 2-bromo-4'-phenyl-acetophenones, 2-bromo-2'-acetophenone (bromomethyl 2-naphthyl ketone), and 1-adamantyl bromomethyl ketone are commercial sources and were used as purchased. 2-(Bromoacetyl)thiophene, 2-(bromoacetyl)-5-chlorothiophene, and bromomethyl *t*-butyl ketone were obtained by bromination of commercially available 2-acetylthiophene, 2-acetyl-5-chlorothiophene, and *t*-butyl methyl ketone, respectively.⁶⁾ 2-(Bromoacetyl)-5-bromothiophene was synthesized by bromination of 2-acetyl-5-bromothiophene which is obtainable from 2-acetylthiophene.

1,5-Diphenyl-3-thiapentane-1,5-dione (**1a**),⁵⁾ 1,5-bis(4-methoxyphenyl)-3-thiapentane-1,5-dione (**1b**),⁵⁾ 1,5-bis(4-methoxyphenyl)-3-thiapentane-1,5-dione (**1c**),⁵⁾ 1,5-bis(4-chlorophenyl)-3-thiapentane-1,5-dione (**1d**),⁵⁾ 1,5-bis(4-bromophenyl)-3-thiapentane-1,5-dione (**1e**),⁵⁾ 1,5-di-2-naphthyl-3-thiapentane-1,5-dione (**1f**),^{1a)} 1,5-di-2-thienyl-3-thiapentane-1,5-dione (**1h**),⁵⁾ and 1,5-di-*t*-butyl-3-thiapentane-1,5-dione (**1k**)⁵⁾ are known compounds.

The following **1** are new compounds.

1,5-Di-4-biphenyl-3-thiapentane-1,5-dione (1g): mp 178–179 °C; white crystals from benzene; ^1H NMR (CDCl_3) δ =4.03 (4H, s, CH_2), 7.4–8.1 (18H, m); ^{13}C NMR (CDCl_3) δ =37.67, 127.27, 128.30, 128.95, 129.22, 134.21, 139.73, 146.24, 193.75; IR (KBr) 1678 cm^{-1} (C=O). Anal. ($\text{C}_{28}\text{H}_{22}\text{O}_2\text{S}$) C, H.

1,5-Bis(5-chloro-2-thienyl)-3-thiapentane-1,5-dione (1i): mp 96–97 °C; pale yellow crystals from ethanol; ^1H NMR (CDCl_3) δ =3.82 (4H, s, CH_2), 6.97 (2H, d, J =4 Hz), 7.57 (2H, d, J =4 Hz); ^{13}C NMR (CDCl_3) δ =36.97, 127.71, 132.69, 140.44, 140.87, 186.27. Anal. ($\text{C}_{12}\text{H}_8\text{Cl}_2\text{O}_2\text{S}_3$) C, H.

1,5-Bis(5-bromo-2-thienyl)-3-thiapentane-1,5-dione (1j): mp 113–114 °C; pale yellow crystals from carbon tetrachloride; ^1H NMR (CDCl_3) δ =3.82 (4H, s, CH_2), 7.11 (2H, d, J =4 Hz), 7.50 (2H, d, J =4 Hz); ^{13}C NMR (CDCl_3) δ =37.13, 123.59, 131.28, 133.12, 143.74, 186.05. Anal. ($\text{C}_{12}\text{H}_8\text{Br}_2\text{O}_2\text{S}_3$) C, H.

1,5-Di-1-adamantyl-3-thiapentane-1,5-dione (1l): mp 81–82 °C; white crystals from methanol; ^1H NMR (CDCl_3) δ =1.62–2.05 (30H, m), 3.49 (4H, broad s, CH_2); IR (KBr)

1704, 1678 cm^{-1} (C=O). Anal. ($\text{C}_{24}\text{H}_{34}\text{O}_2\text{S}$) C, H.

General Procedure for the Preparation of 2,7-Dihydro-1,4,5-thiadiazepines (2). A mixture of a 3-thiapentane-1,5-dione (**1**; 10 mmol) and hydrazine monohydrate (16 mmol) in ethanol (50–100 ml) containing *p*-toluenesulfonic acid monohydrate (ca. 10 mg) was heated under reflux until the starting sulfide had disappeared. The mixture was cooled to room temperature and the resulting crystalline precipitate was collected by filtration, washed with a small amount of cold ethanol, and recrystallized from an appropriate solvent.

Only compound **2g** was prepared by heating **1g** (5 mmol) and hydrazine monohydrate (8 mmol) in acetic acid (150 ml) at 95 °C for 2 h.

3,6-Diphenyl-2,7-dihydro-1,4,5-thiadiazepine (2a): mp 181–182 °C (lit.³ mp 174–175 °C); white fine needles from ethanol; ^1H NMR (CDCl_3) δ =3.22 (2H, d, J =12 Hz), 3.54 (2H, d, J =12 Hz), 7.21–7.43 (6H, m), 7.69–7.81 (4H, m); ^{13}C NMR (CDCl_3) δ =26.46, 127.17, 128.79, 130.15, 135.18, 151.65.

3,6-Bis(4-methylphenyl)-2,7-dihydro-1,4,5-thiadiazepine (2b): mp 206–207 °C (lit.³ mp 215 °C); white crystals from carbon tetrachloride; ^1H NMR (CDCl_3) δ =2.41 (6H, s), 3.33 (2H, d, J =13 Hz), 3.64 (2H, d, J =13 Hz), 7.27 (4H, d, J =8 Hz), 7.79 (4H, d, J =8 Hz); ^{13}C NMR (CDCl_3) δ =21.31, 26.35, 127.06, 129.50, 132.42, 140.33, 151.54.

3,6-Bis(4-methoxyphenyl)-2,7-dihydro-1,4,5-thiadiazepine (2c): mp 214–215 °C; white needles from benzene; ^1H NMR (CDCl_3) δ =3.31 (2H, d, J =13 Hz), 3.61 (2H, d, J =13 Hz), 3.87 (6H, s), 6.97 (4H, d, J =9 Hz), 7.84 (4H, d, J =9 Hz); ^{13}C NMR (CDCl_3) δ =26.29, 55.44, 114.27, 127.76, 128.63, 151.27, 161.30; IR (Nujol) 1600, 1546, 1506, 1302, 1254, 1176, 1018, 842 cm^{-1} ; UV/Vis (CH_2Cl_2) 282 (ϵ =18000), 316 nm (sh, 15000). Anal. ($\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2\text{S}$) C, H, N.

3,6-Bis(4-chlorophenyl)-2,7-dihydro-1,4,5-thiadiazepine (2d): mp 195–196 °C; white needles from carbon tetrachloride; ^1H NMR (CDCl_3) δ =3.20 (2H, d, J =13 Hz), 3.68 (2H, d, J =13 Hz), 7.43 (4H, d, J =9 Hz), 7.83 (4H, d, J =9 Hz); ^{13}C NMR (CDCl_3) δ =26.29, 128.41, 129.06, 133.40, 136.38, 150.62; IR (Nujol) 1650, 1592, 1492, 1318, 1090, 1008, 896, 832 cm^{-1} ; UV/Vis (CH_2Cl_2) 276 (ϵ =17000), 316 nm (9200). Anal. ($\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{N}_2\text{S}$) C, H, N.

3,6-Bis(4-bromophenyl)-2,7-dihydro-1,4,5-thiadiazepine (2e): mp 208–209 °C (lit.³ mp 202 °C); white fine needles from ethanol; ^1H NMR (CDCl_3) δ =3.29 (2H, d, J =13 Hz), 3.62 (2H, d, J =13 Hz), 7.58 (4H, d, J =8.5 Hz), 7.76 (4H, d, J =8.5 Hz); ^{13}C NMR (CDCl_3) δ =26.29, 128.57, 132.04, 133.83, 143.37, 150.68.

3,6-Di-2-naphthyl-2,7-dihydro-1,4,5-thiadiazepine (2f): mp 223–224 °C; white needles from carbon tetrachloride; ^1H NMR (CDCl_3) δ =3.57 (2H, d, J =13 Hz), 3.80 (2H, d, J =13 Hz), 7.52–7.57 (4H, m), 7.87–7.95 (6H, m), 8.14–8.17 (2H, m), 8.28 (2H, s); IR (Nujol) 1598, 1550, 1316, 1150, 858, 822, 748 cm^{-1} ; UV/Vis (CH_2Cl_2) 264 (ϵ =33000), 316 nm (sh, 16000). HRMS Found: m/z 366.1193. Calcd for $\text{C}_{24}\text{H}_{18}\text{N}_2\text{S}$: M, 366.1191.

3,6-Di-4-biphenyl-2,7-dihydro-1,4,5-thiadiazepine (2g): mp 267 °C (decomp); white crystals from chloroform ^1H NMR (CDCl_3) δ =3.51 (2H, d, J =13 Hz), 3.65 (2H, d, J =13 Hz), 7.40–8.05 (18H, m); IR (KBr) 1604, 1572, 1488, 1438, 1326, 844, 762, 734, 688 cm^{-1} ; UV/Vis (CH_2Cl_2) 296 (ϵ =36000), 322 nm (sh, 34000). HRMS Found: m/z 418.1501. Calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{S}$: M, 418.1503.

3,6-Di-2-thienyl-2,7-dihydro-1,4,5-thiadiazepine (2h): mp

198–199 °C; pale yellow crystals from benzene/hexane; ^1H NMR (CDCl_3) δ =3.47 (2H, d, J =13 Hz), 3.62 (2H, d, J =13 Hz), 7.04–7.14 (2H, m), 7.36–7.50 (4H, m); ^{13}C NMR (CDCl_3) δ =26.83, 127.54, 129.71, 139.79, 148.13; IR (KBr) 3072, 1556, 1438, 1310, 1148, 1058, 1016, 856 cm^{-1} ; UV/Vis (CH_2Cl_2) 276 (ϵ =15000), 318 nm (14000); MS m/z 278 (M^+). Anal. ($\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_3$) C, H, N.

3,6-Bis(5-chloro-2-thienyl)-2,7-dihydro-1,4,5-thiadiazepine (2i): mp 209–210 °C; pale yellow crystals from ethanol; ^1H NMR (CDCl_3) δ =3.41 (2H, d, J =12.5 Hz), 3.55 (2H, d, J =12.5 Hz), 6.91 (2H, d, J =4 Hz), 7.14 (2H, d, J =4 Hz); IR (Nujol) 1558, 1528, 1324, 1214, 1008, 816, 726, 698 cm^{-1} . UV/Vis (CH_2Cl_2) 294 (ϵ =14000), 348 nm (19000); MS m/z , M^+ (relative intensity) 346 (100), 347 (15), 348 (70), 349 (11), 350 (21). Anal. ($\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_2\text{S}_3$) C, H, N.

3,6-Bis(5-bromo-2-thienyl)-2,7-dihydro-1,4,5-thiadiazepine (2j): mp 180 °C (decomp); pale yellow crystals from benzene; ^1H NMR (CDCl_3) δ =3.24 (2H, d, J =13 Hz), 3.78 (2H, d, J =13 Hz), 7.05 (2H, d, J =4 Hz), 7.11 (2H, d, J =4 Hz); IR (Nujol) 3092, 1558, 1436, 1320, 1214, 1070, 1018, 982, 818 cm^{-1} UV/Vis (CH_2Cl_2) 296 (ϵ =19000), 345 nm (25000). HRMS Found: m/z 435.8229. Calcd for $\text{C}_{12}\text{H}_8^{79}\text{Br}^{81}\text{BrN}_2\text{S}_3$: M, 435.8196.

3,6-Di-*t*-butyl-2,7-dihydro-1,4,5-thiadiazepine (2k): mp 144–145 °C; white flakes from ethanol; ^1H NMR (CDCl_3) δ =1.26 (18H, s), 2.86 (2H, d, J =12 Hz), 3.02 (2H, d, J =12 Hz); ^{13}C NMR (CDCl_3) δ =23.75, 28.03, 37.83, 160.54; IR (KBr) 2976, 2924, 1590, 1462, 1422, 1360, 1176, 1070, 904, 720 cm^{-1} . Anal. ($\text{C}_{12}\text{H}_{22}\text{N}_2\text{S}$) C, H, N.

3,6-Di-1-adamantyl-2,7-dihydro-1,4,5-thiadiazepine (2l): mp 271–272 °C; white prisms from benzene/hexane; ^1H NMR (CDCl_3) δ =1.60–2.05 (30H, m), 2.88 (2H, d, J =12 Hz), 3.02 (2H, d, J =12 Hz); ^{13}C NMR (CDCl_3) δ =22.95, 29.19, 36.71, 39.80, 40.09, 160.79; IR (KBr) 2904, 2848, 1582, 1450, 1342, 1280, 1250, 1100, 1028, 838 cm^{-1} ; UV/Vis (CH_2Cl_2) 268 nm (ϵ =20000); MS m/z 382 (M^+). Anal. ($\text{C}_{24}\text{H}_{34}\text{N}_2\text{S}$) C, H, N.

General Procedure for the Preparation of 3,6-Disubstituted Pyridazines (3) from 2,7-Dihydro-1,4,5-thiadiazepines (2). A suspension of a 2,7-dihydro-1,4,5-thiadiazepine (**2**, 1 mmol) in diethylene glycol (10 ml) was heated under reflux until the starting **1** had been completely consumed (for the time of refluxing, see the Scheme 1). The evolution of hydrogen sulfide during the reaction was observed in every case. The mixture was cooled to room temperature and the resulting crystalline precipitate of **3** was collected by filtration, washed with a small amount of cold methanol or ethanol, and recrystallized from an appropriate solvent. The original filtrate and washings were combined, diluted with water, and extracted with dichloromethane. The extract was purified by column chromatography on silica gel to give an additional amount of **3**.

3,6-Diphenylpyridazine (3a): mp 222–223 °C (lit.³ mp 222 °C); ^1H NMR (CDCl_3) δ =7.40–8.20 (10H, m), 7.87 (2H, s); ^{13}C NMR (CDCl_3) δ =126.62, 128.30, 129.01, 136.21, 138.54, 157.67.

3,6-Bis(4-methylphenyl)pyridazine (3b): mp 231–232 °C (lit.³ mp 236 °C); ^1H NMR (CDCl_3) δ =2.43 (6H, s), 7.33 (4H, d, J =8 Hz), 7.86 (2H, s), 8.04 (4H, d, J =8 Hz) ^{13}C NMR (CDCl_3) δ =21.25, 123.75, 126.73, 129.71, 133.45, 140.06, 157.34.

3,6-Bis(4-methoxyphenyl)pyridazine (3c): mp 238–240 °C (lit.¹⁰ mp 235 °C); ^1H NMR (CDCl_3) δ =3.89 (6H, s),

7.06 (4H, d, $J=9$ Hz), 7.83 (2H, s), 8.11 (4H, d, $J=9$ Hz).

3,6-Bis(4-chlorophenyl)pyridazine (3d): mp 265–267 °C (lit.¹¹) mp 264 °C; ^1H NMR (CDCl_3) $\delta=7.52$ (4H, d, $J=9$ Hz), 7.91 (2H, s), 8.11 (4H, d, $J=9$ Hz).

3,6-Bis(4-bromophenyl)pyridazine (3e): mp 285–286 °C (lit.³) mp 288 °C; ^1H NMR (CDCl_3) $\delta=7.68$ (4H, d, $J=9$ Hz), 7.91 (2H, s), 8.04 (4H, d, $J=9$ Hz).

3,6-Di-2-naphthylpyridazine (3f): mp 280–281 °C; pale yellow crystals from 1,2-dichloroethane; ^1H NMR (CDCl_3) $\delta=7.56$ –7.58 (4H, m), 7.92–7.94 (2H, m), 7.99–8.05 (4H, m), 8.15 (2H, s), 8.36–8.39 (2H, m), 8.67 (2H, s). HRMS Found: m/z 332.1311. Calcd for $\text{C}_{24}\text{H}_{16}\text{N}_2$: M, 332.1314.

3,6-Di-4-biphenylpyridazine (3g): mp 357–359 °C; white powder (purified by sublimation at 345–350 °C/0.01 Torr); ^1H NMR (CDCl_3) $\delta=7.38$ –8.26 (18H, m), 8.01 (2H, s); IR (KBr) 1584, 1486, 1418, 1166, 1040, 1002, 828, 758, 718, 682, 582, 472 cm^{-1} . Anal. ($\text{C}_{28}\text{H}_{20}\text{N}_2$) C, H, N.

3,6-Di-2-thienylpyridazine (3h): mp 181–182 °C (lit.¹²) mp 175–176 °C; ^1H NMR (CDCl_3) $\delta=7.13$ (2H, dd, $J=5$, 4 Hz), 7.47 (2H, dd, $J=5$, 1 Hz), 7.63 (2H, dd, $J=4$, 1 Hz), 7.71 (2H, s).

3,6-Bis(5-chloro-2-thienyl)pyridazine (3i): mp >300 °C (decomp); yellow crystals from benzene; IR (KBr) 1554, 1444, 1122, 1014, 838, 788, 530, 456 cm^{-1} ; MS m/z , M^+ (relative intensity) 312 (100), 314 (85), 316 (25). Anal. ($\text{C}_{12}\text{H}_6\text{Cl}_2\text{N}_2\text{S}_2$) C, H, N.

3,6-Bis(5-bromo-2-thienyl)pyridazine (3j): mp >300 °C (decomp); yellow crystals from benzene; IR (KBr) 1552, 1436, 1122, 838, 790, 746, 586 cm^{-1} . HRMS Found: m/z 401.8309. Calcd for $\text{C}_{12}\text{H}_6^{79}\text{Br}^{81}\text{BrN}_2\text{S}_2$: M, 401.8318.

3,6-Di-*t*-butylpyridazine (3k): mp 179–180 °C; white crystals from pentane; ^1H NMR (CDCl_3) $\delta=1.44$ (18H, s), 7.44 (2H, s); ^{13}C NMR (CDCl_3) $\delta=30.00$, 36.53, 123.10, 167.58; IR (KBr) 2972, 1588, 1538, 1482, 1366, 1152, 1038, 872 cm^{-1} . Anal. ($\text{C}_{12}\text{H}_{20}\text{N}_2$) C, H.

3,6-Di-1-adamantylpyridazine (3l): mp 278–280 °C; white crystals from methanol; ^1H NMR (CDCl_3) $\delta=1.61$ –2.08 (30H, m), 7.37 (2H, s); ^{13}C NMR (CDCl_3) $\delta=28.68$, 36.70, 38.16, 41.73, 122.72, 167.25; IR (KBr) 2904, 2848, 1582, 1452, 1422, 1312, 1056, 810 cm^{-1} . Anal. ($\text{C}_{24}\text{H}_{32}\text{N}_2$) C, H, N.

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