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2,3-Dihydro-5H-1,4-benzoxathiepins were prepared by intramolecular Friedel-Crafts reactions of ethyl  $\alpha$ -[2-(aryloxy)ethylthio]- $\alpha$ -chloroacetates or by acid-catalyzed cyclizations of ethyl  $\alpha$ -[2-(aryloxy)ethylsulfinyl]-acetate. 1,2,3,5-Tetrahydro-4,1-benzothiazepines were similarly prepared.

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The condensed seven-membered heterocycles have been the subject of intensive synthetic studies since they possess a wide spectrum of pharmacological activities. In a series of papers [1a-c] we reported the syntheses of the condensed five- and six-membered heterocycles by the following two methods: i) intramolecular Friedel-Crafts reaction of arenes with  $\alpha$ -acyl- $\alpha$ -chlorosulfides (Method A) and ii) acid-catalyzed aromatic cyclization of  $\alpha$ -acylsulfoxides (Method B). We now describe a further extension of the methods to the synthesis of the condensed seven-membered heterocycles such as 2,3-dihydro-5H-1,4-benzoxathiepins and 1,2,3,5-tetrahydro-4,1-benzothiazepines.

The following procedures for the preparations of the 1,4-benzoxathiepin **4a** and the 4,1-benzothiazepine **4d** are representative.

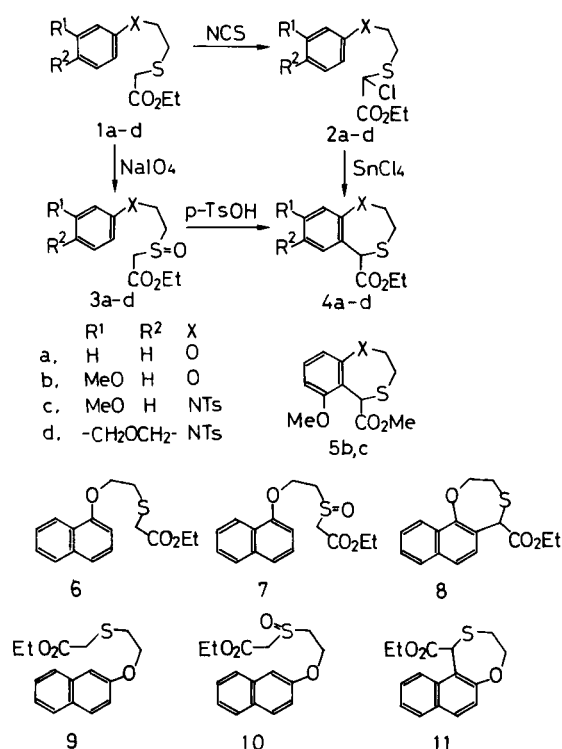
Method A: Treatment of the chloride **2a**, which was prepared *in situ* from the sulfide **1a** and *N*-chlorosuccinimide, with stannic chloride in methylene chloride at room temperature gave the 1,4-benzoxathiepin **4a** in 22% yield (based on **1a**).

Method B: Treatment of the sulfoxide **3d**, which was prepared by oxidation of the sulfide **1d** with sodium metaperiodate, with *p*-toluenesulfonic acid in boiling benzene yielded the 4,1-benzothiazepine **4d** in 76% yield.

Table 1  
Preparation of **1a-d**, **3a-d**, **6**, **7**, **9** and **10**

| Compound      | Yield,<br>% | IR $\nu$ cm <sup>-1</sup><br>(chloroform) | Formula   | Analysis, % |      |      |
|---------------|-------------|---|---|-------------|------|------|
|               |             |   |   | C           | H    | N    |
| <b>1a</b>     | 82          | 1730                                      | C <sub>12</sub> H <sub>16</sub> O <sub>3</sub> S                                    | 59.98       | 6.71 |      |
|               |             |   |   | 60.09       | 6.66 |      |
| <b>1b</b>     | 46          | 1725                                      | C <sub>13</sub> H <sub>18</sub> O <sub>4</sub> S                                    | 57.76       | 6.71 |      |
|               |             |   |   | 57.74       | 6.78 |      |
| <b>1c</b>     | 55          | 1730                                      | C <sub>20</sub> H <sub>25</sub> NO <sub>5</sub> S <sub>2</sub>                      | 56.72       | 5.95 | 3.31 |
|               |             |   |   | 56.96       | 5.92 | 3.33 |
| <b>1d</b>     | 64          | 1730                                      | C <sub>20</sub> H <sub>23</sub> NO <sub>6</sub> S <sub>2</sub>                      | 54.90       | 5.30 | 3.20 |
|               |             |   |   | 54.75       | 5.29 | 3.11 |
| <b>3a</b> [a] | 88          | 1730                                      | C <sub>12</sub> H <sub>16</sub> O <sub>4</sub> S                                    | 56.23       | 6.29 |      |
|               |             |   |   | 56.24       | 6.22 |      |
| <b>3b</b>     | 84          | 1730                                      | C <sub>13</sub> H <sub>18</sub> O <sub>5</sub> S                                    | 54.53       | 6.34 |      |
|               |             |   |   | 54.29       | 6.49 |      |
| <b>3c</b> [b] | 62          | 1730                                      | C <sub>20</sub> H <sub>25</sub> NO <sub>6</sub> S <sub>2</sub>                      | 54.65       | 5.73 | 3.19 |
|               |             |   |   | 54.68       | 5.68 | 3.38 |
| <b>3d</b>     | 54          | 1735                                      | C <sub>20</sub> H <sub>23</sub> NO <sub>7</sub> S <sub>2</sub> ·1/4H <sub>2</sub> O | 52.44       | 5.17 | 3.06 |
|               |             |   |   | 52.02       | 5.17 | 2.85 |
| <b>6</b>      | 66          | 1730                                      | C <sub>16</sub> H <sub>18</sub> O <sub>3</sub> S                                    | 66.18       | 6.25 |      |
|               |             |   |   | 66.41       | 6.41 |      |
| <b>7</b>      | 71          | 1730                                      | C <sub>16</sub> H <sub>18</sub> O <sub>4</sub> S·1/4H <sub>2</sub> O                | 61.84       | 5.96 |      |
|               |             |   |   | 61.95       | 5.82 |      |
| <b>9</b>      | 38          | 1730                                      | C <sub>16</sub> H <sub>18</sub> O <sub>3</sub> S                                    | 66.18       | 6.25 |      |
|               |             |   |   | 65.92       | 6.26 |      |
| <b>10</b> [c] | 79          | 1730                                      | C <sub>16</sub> H <sub>18</sub> O <sub>4</sub> S·1/4H <sub>2</sub> O                | 61.84       | 5.96 |      |
|               |             |   |   | 62.11       | 5.78 |      |

[a] mp 64.5-65.0° (from benzene). [b] mp 88.5-89.0° (from *n*-hexane/ethyl acetate). [c] mp 89.5-90.0° (from *n*-hexane).

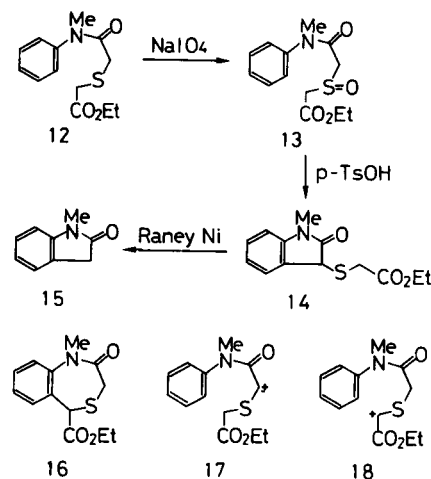


Scheme 1

Other 1,4-benzoxathiepin derivatives **8** and **11** were similarly prepared. The cyclizations of the chlorides **2b** and **2c** afforded mixtures of two regioisomers **4b,5b** and **4c,5c**, respectively. Similar results were obtained by cyclizations of the sulfoxides **3b** and **3c**. As can be seen from the Table 3, Method B is generally superior to Method A except for a few cases.

The structural determination of the cyclized products were made by examination of their  $^1\text{H}$  nmr spectra. The signals ascribable to the benzylic methine protons,  $-\text{S}-\text{CH}-\text{COOEt}$ , of the products **4a-d** and **8** appear as singlets at  $\delta$  4.64 to 4.87, whereas the low-field shifts are observed for the corresponding methine protons of the compounds **5b** ( $\delta$  5.18), **5c** ( $\delta$  5.17) and **11** ( $\delta$  5.32), presumably due to the deshielding effect of a neighboring (*ortho*) methoxy group (for **5b,c**) and the peri effect (for **11**), respectively.

Finally, in an attempt to prepare the 3,5-dihydro-4,1-benzothiazepin-2(1*H*)-one derivative such as **16**, we treated the sulfoxide **13** with *p*-toluenesulfonic acid in boiling benzene. Unfortunately the reaction afforded only the oxindole derivative **14** in 60% yield. This may be a result of formation of the carbenium ion **17** rather than an expected carbenium ion **18** by the Pummerer reaction of the sulfoxide **13**. The structure of **14** was confirmed by transforming it to the oxindole **15** by desulfurization with Raney nickel.



Scheme 2

Table 2

Proton Magnetic Resonance Parameters for **1a-d**, **3a-d**, **6**, **7**, **9** and **10**

| Compound  | Chemical shift (deuteriochloroform) $\delta$ (ppm)   |
|-----------|--|
| <b>1a</b> | 1.17 (t, 3H, J = 7 Hz), 2.92 (t, 2H, J = 6.4 Hz), 3.24 (2, 2H), 4.07 (t, 2H, J = 6.4 Hz), 4.09 (q, 2H, J = 7 Hz), 6.5-7.4 (m, 5H)  |
| <b>1b</b> | 1.25 (t, 3H, J = 7 Hz), 2.99 (t, 2H, J = 6.2 Hz), 3.31 (s, 2H), 3.75 (s, 3H), 4.13 (t, 2H, J = 6.2 Hz), 4.15 (q, 2H, J = 7 Hz), 6.3-6.7 (m, 3H), 7.0-7.4 (m, 1H)                                 |
| <b>1c</b> | 1.23 (t, 3H, J = 7 Hz), 2.40 (s, 3H), 2.6-3.0 (m, 2H), 3.17 (s, 2H), 3.5-3.9 (m, 2H), 3.71 (s, 3H), 4.16 (q, 2H, J = 7 Hz), 6.4-7.3 (m, 6H), 7.49 (d, 2H, J = 8 Hz)                              |
| <b>1d</b> | 1.23 (t, 3H, J = 7 Hz), 2.40 (s, 3H), 2.5-2.9 (m, 2H), 3.18 (s, 2H), 3.6-3.9 (m, 2H), 4.12 (q, 2H, J = 7 Hz), 5.91 (s, 2H), 6.3-6.8 (m, 5H), 7.26, 7.56 (AB q, 2H, J = 8 Hz)                     |
| <b>3a</b> | 1.30 (t, 3H, J = 7 Hz), 3.1-3.4 (m, 2H), 3.75, 3.83 (AB q, 2H, J = 14 Hz), 4.22 (q, 2H, J = 7 Hz), 4.40 (t, 2H, J = 5.5 Hz), 6.7-7.5 (m, 5H)   |
| <b>3b</b> | 1.30 (t, 3H, J = 7 Hz), 3.2-3.5 (m, 2H), 3.76 (s, 3H), 3.77, 3.83 (AB q, 2H, J = 14 Hz), 4.25 (q, 2H, J = 7 Hz), 4.43 (t, 2H, J = 5.8 Hz), 6.4-6.7 (m, 3H), 7.0-7.4 (m, 1H)                      |
| <b>3c</b> | 1.26 (t, 3H, J = 7 Hz), 2.40 (s, 3H), 3.10 (br t, 2H, J = 6 Hz), 3.70 (s, 3H), 3.8-4.1 (m, 2H), 4.17 (q, 2H, J = 7 Hz), 6.4-7.2 (m, 7H), 7.25, 7.49 (AB q, 2H, J = 8 Hz)                         |
| <b>3d</b> | 1.23 (t, 3H, J = 7 Hz), 2.40 (s, 3H), 3.09 (br t, 2H, J = 6 Hz), 3.71 (s, 2H), 3.93 (br t, 2H, J = 6 Hz), 4.20 (q, 2H, J = 7 Hz), 5.91 (s, 2H), 6.3-6.8 (m, 5H), 7.26, 7.50 (AB q, 2H, J = 8 Hz) |
| <b>6</b>  | 1.23 (t, 3H, J = 7 Hz), 3.13 (t, 2H, J = 6.2 Hz), 3.33 (s, 2H), 4.13 (q, 2H, J = 7 Hz), 4.29 (t, 2H, J = 6.2 Hz), 6.70 (dd, 1H, J = 6, 3 Hz), 7.1-7.9 (m, 5H), 8.1-8.4 (m, 1H)                   |
| <b>7</b>  | 1.26 (t, 3H, J = 7 Hz), 3.2-3.5 (m, 2H), 3.77, 3.85 (AB q, 2H, J = 14 Hz), 4.15 (q, 2H, J = 7 Hz), 4.56 (t, 2H, J = 5.5 Hz), 6.78 (dd, 1H, J = 6, 3 Hz), 7.1-7.9 (m, 5H), 8.0-8.3 (m, 1H)        |
| <b>9</b>  | 1.21 (t, 3H, J = 7 Hz), 2.8-3.2 (m, 2H), 3.29 (s, 2H), 3.9-4.3 (m, 4H), 7.0-7.9 (m, 7H)  |
| <b>10</b> | 1.28 (t, 3H, J = 7 Hz), 3.2-3.5 (m, 2H), 3.80, 3.93 (AB q, 2H, J = 14 Hz), 4.22 (q, 2H, J = 7 Hz), 4.55 (t, 2H, J = 5.5 Hz), 7.0-7.9 (m, 7H)   |

Table 3  
Preparation of **4a-d**, **5b,c**, **8** and **11**

| Compound       | Method A | Method B | Yield, %<br>IR $\nu$ $\text{cm}^{-1}$<br>(chloroform) | Formula   | Analysis, % |      |      |
|----------------|----------|----------|---|---|-------------|------|------|
|                |          |          |   |   | C           | H    | N    |
| <b>4a</b>      | 22       | [a]      | 1730  | $\text{C}_{12}\text{H}_{14}\text{O}_3\text{S}$    | 60.48       | 5.92 |      |
|                |          |          |   |   | 60.71       | 6.02 |      |
| <b>4b + 5b</b> | 28       | 53       | 1730  | $\text{C}_{13}\text{H}_{16}\text{O}_4\text{S}$    | 58.19       | 6.01 |      |
|                |          |          |   |   | 57.96       | 6.23 |      |
| <b>4c</b>      | 33       | 55       | 1730  | $\text{C}_{20}\text{H}_{23}\text{NO}_5\text{S}_2$ | 56.99       | 5.50 | 3.32 |
|                |          |          |   |   | 56.70       | 5.74 | 3.56 |
| <b>5c [b]</b>  | 22       | 36       | 1730  | $\text{C}_{20}\text{H}_{23}\text{NO}_5\text{S}_2$ | 56.99       | 5.50 | 3.32 |
|                |          |          |   |   | 56.47       | 5.46 | 3.22 |
| <b>4d [c]</b>  | 61       | 76       | 1730  | $\text{C}_{20}\text{H}_{21}\text{NO}_6\text{S}_2$ | 55.16       | 4.86 | 3.22 |
|                |          |          |   |   | 54.94       | 4.70 | 3.51 |
| <b>8 [d]</b>   | [a]      | 27       | 1730  | $\text{C}_{16}\text{H}_{16}\text{O}_3\text{S}$    | 66.64       | 5.59 |      |
|                |          |          |   |   | 66.43       | 5.59 |      |
| <b>11</b>      | 20       | 21       | 1730  | $\text{C}_{16}\text{H}_{16}\text{O}_3\text{S}$    | 66.64       | 5.59 |      |
|                |          |          |   |   | 66.88       | 5.67 |      |

[a] A complex mixture of products was obtained. [b] mp 158-159° (from ethyl acetate/*n*-hexane). [c] mp 144.5-145.0° (from ethanol). [d] mp 108.0-108.5° (from *n*-hexane).

Table 4

Proton Magnetic Resonance Parameters for **4a-d**, **5b,c**, **8** and **11**

| Compound       | Chemical shift (deuteriochloroform) $\delta$ (ppm)   |
|----------------|--|
| <b>4a</b>      | 1.24 (t, 3H, J = 7 Hz), 2.7-3.2 (m, 2H), 3.9-4.5 (m, 2H), 4.20 (q, 2H, J = 7 Hz), 4.73 (s, 1H), 6.6-7.6 (m, 4H)  |
| <b>4b + 5b</b> | 1.20, 1.23 (t x 2, total 3H, J = 7 Hz), 2.6-3.4 (m, 2H), 3.76, 3.81 (s x 2, total 3H), 4.0-4.5 (m, 4H), 4.64, 5.18 (s x 2, total 1H), 6.3-7.4 (m, 3H)                        |
| <b>4c</b>      | 1.28 (t, 3H, J = 7 Hz), 2.43 (s, 3H), 2.7-3.7 (m, 4H), 3.68 (s, 3H), 4.24 (q, 2H, J = 7 Hz), 4.67 (s, 1H), 6.6-7.3 (m, 3H), 7.32, 7.67 (AB q, 2H, J = 8 Hz)                  |
| <b>5c</b>      | 1.25 (t, 3H, J = 7 Hz), 2.43 (s, 3H), 2.6-4.5 (m, 6H), 3.81 (s, 3H), 5.17 (br s, 1H), 6.5-7.0 (m, 3H), 7.26, 7.70 (AB q, 2H, J = 7 Hz)                                       |
| <b>4d</b>      | 1.27 (t, 3H, J = 7 Hz), 2.41 (s, 3H), 2.5-3.6 (m, 4H), 4.21 (q, 2H, J = 7 Hz), 4.64 (br s, 1H), 5.90 (s, 2H), 6.57 (br s, 1H), 6.61 (s, 1H), 7.33, 7.67 (AB q, 2H, J = 8 Hz) |
| <b>8</b>       | 1.24 (t, 3H, J = 5.7 Hz), 2.6-3.6 (m, 2H), 4.1-4.4 (m, 2H), 4.23 (q, 2H, J = 7 Hz), 4.87 (s, 1H), 7.1-7.9 (m, 5H), 8.0-8.3 (m, 1H)   |
| <b>11</b>      | 1.16 (t, 3H, J = 5.7 Hz), 2.3-3.7 (m, 2H), 3.8-4.8 (m, 2H), 4.21 (q, 2H, J = 7 Hz), 5.32 (s, 1H), 7.1-8.0 (m, 6H)  |

## EXPERIMENTAL

All melting points are uncorrected. The ir spectra were recorded with a JASCO-IRA-1 spectrophotometer. The  $^1\text{H}$  nmr spectra were determined on a JEOL JNM-PMX 60 spectrometer using tetramethylsilane as an internal standard.

2-(3,4-Methylenedioxyphenylamino)ethanol.

2-Chloroethanol (2.4 g, 30 mmoles) was added dropwise to a stirred

mixture of sodium hydroxide (8 g, 0.2 moles) and 3,4-(methylenedioxy)aniline (5.5 g, 40 mmoles) in water (40 ml) and ethanol (20 ml) at 60° and the mixture was further stirred at the same temperature for 1 hour. After cooling, the reaction mixture was made to pH 8 by addition of dilute hydrochloric acid and extracted with benzene, dried over magnesium sulfate. The solvent was removed by evaporation and the residue was chromatographed on silica gel using benzene/ethyl acetate (1:1) as eluent to give 2-(3,4-methylenedioxyphenylamino)ethanol (2.3 g, 32% yield), mp 74.5-75° (from benzene/ethyl acetate);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.93 (br s, 1H), 3.13 (br t, 2H, J = 5 Hz), 3.73 (br t, 2H, J = 5 Hz), 5.77 (s, 2H), 6.02 (dd, 1H, J = 8, 2 Hz), 6.18 (d, 1H, J = 2 Hz), 6.58 (d, 1H, J = 8 Hz).

Anal. Calcd. for  $\text{C}_9\text{H}_{11}\text{NO}_3$ : C, 59.66; H, 6.12; N, 7.73. Found: C, 59.69; H, 6.38; N, 7.72.

Ethyl (2-Phenoxyethylthio)acetate (**1a**), Ethyl [2-(3-Methoxyphenoxy)ethylthio]acetate (**1b**), Ethyl [2-(1-Naphthoxy)ethylthio]acetate (**6**) and Ethyl [2-(2-Naphthoxy)ethylthio]acetate (**9**). General Procedure.

Ethyl thioglycolate (6.0 g, 50 mmoles) and (2-bromoethoxy)benzene (Aldrich Chemical Co., Inc.), 1-(2-bromoethoxy)-3-methoxybenzene [**2**], 1-(2-bromoethoxy)naphthalene [**3**] or 2-(2-bromoethoxy)naphthalene [**4**] (50 mmoles) were successively added to a solution of sodium ethoxide (3.4 g 50 mmoles) in absolute ethanol (70 ml) at room temperature and the mixture was heated under reflux for 5 hours. After removal of the solvent, the residue was poured into water and extracted with benzene, then dried over magnesium sulfate. The solvent was evaporated off and the residue was chromatographed on silica gel using benzene as eluent to give the sulfide **1a** (82%), **1b** (46%), **6** (66%) or **9** (38%), whose physical data are given in Tables 1 and 2.

Ethyl [2-[N-(3-Methoxyphenyl)-N-(4-methylphenylsulfonyl)amino]ethylthio]acetate (**1c**) and Ethyl [2-[N-(3,4-Methylenedioxyphenyl)-N-(4-methylphenylsulfonyl)amino]ethylthio]acetate (**1d**). General Procedure.

2-(3-Methoxyphenylamino)ethanol [**5**] or 2-(3,4-methylenedioxyphenylamino)ethanol was *N,O*-ditosylated by an usual method (*p*-toluene-sulfonyl chloride, pyridine) and the resultant crude *N,O*-ditosylate (50 mmoles) was added to a solution of sodium ethoxide (3.4 g, 50 mmoles) in absolute ethanol (70 ml) at room temperature. The mixture was heated under reflux for 5 hours and the solvent was removed by evaporation.

The residue was poured into water and extracted with benzene, dried over magnesium sulfate. The solvent was evaporated off and the residue was chromatographed on silica gel using *n*-hexane/ethyl acetate (2:1) as eluent to give the sulfide **1c** (55%) or **1d** (64%), whose physical data are given in Tables 1 and 2.

#### Sulfoxides **3a-d**, **7** and **10**. General Procedure.

To a solution of the sulfide **1a-d**, **6** or **9** (4 mmoles) in methanol (50 ml) was added dropwise to a solution of sodium metaperiodate (856 mg, 4 mmoles) in water (20 ml) at 0° and the mixture was stirred at room temperature for 15 hours. The precipitated inorganic materials were filtered off and the filtrate was extracted with methylene chloride, then dried over magnesium sulfate. The solvent was evaporated off and the residue was chromatographed on silica gel using benzene/ethyl acetate (1:1) as eluent to give the sulfoxide **3a** (88%), **3b** (84%), **3c** (62%), **3d** (54%), **7** (71%) or **10** (79%), whose physical data are given in Tables 1 and 2.

#### Preparation of **4a-d**, **5b,c**, **8** and **11**.

**Method A:** To a stirred solution of the sulfide **1a-d**, **6** or **9** (1 mmole) in carbon tetrachloride (8 ml) was added *N*-chlorosuccinimide (140 mg, 1 mmole) at 0°C and the mixture was stirred at room temperature for 10 hours. After removal of the precipitated succinimide, the solvent was evaporated off and the resultant crude chloride (*e.g.*, **2a-d**) was again dissolved in methylene chloride (10 ml). Stannic chloride (261 mg, 1 mmole) was then added to the solution *via* a syringe at 0° and the mixture was stirred at room temperature for 1 hour. The reaction was quenched by addition of water (10 ml) and the organic layer was separated. The aqueous layer was further extracted with methylene chloride and a combined organic layer was dried over magnesium sulfate. The solvent was evaporated off and the residue was chromatographed on silica gel using benzene/ethyl acetate (5:1) as eluent to give **4a-d**, **5b,c** or **11**, whose yields and physical data are given in Tables 3 and 4, respectively.

**Method B:** To a solution of anhydrous *p*-toluenesulfonic acid (344 mg, 2 mmoles) in dry benzene (20 ml) was added a solution of the sulfoxide **3a-d**, **7** or **10** (1 mmole) in dry benzene (3 ml) and the mixture was heated under reflux for 1 hour. After cooling, the mixture was washed and dried over magnesium sulfate. The solvent was evaporated off and the residue was chromatographed on silica gel using benzene/ethyl acetate (5:1) as eluent to give **4a-d**, **5b,c**, **8** or **11**, whose yields and physical data are given in Tables 3 and 4, respectively.

#### $\alpha$ -(Ethoxycarbonylmethylthio)-*N*-methylacetanilide (**12**).

To a stirred solution of *N*-methylaniline (268 mg, 2.5 mmoles) in methylene chloride (10 ml) containing triethylamine (253 mg, 2.5 mmoles) was added dropwise (ethoxycarbonylmethylthio)acetyl chloride (492 mg, 2.5 mmoles) at 0° and the mixture was stirred at room temperature for 30 minutes. The precipitated triethylamine hydrochloride was filtered off and the filtrate was washed with dilute hydrochloric acid, then dried over magnesium sulfate. The solvent was removed by evaporation and the residue was chromatographed on silica gel using benzene/ethyl acetate (2:1) as eluent to give **12** (441 mg, 66%), mp

41-42° (from petolorium ether) ir (chloroform): 1730, 1640 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.25 (t, 3H, J = 7 Hz), 3.20 (br s, 2H), 3.28 (s, 3H), 3.40 (s, 2H), 4.15 (q, 2H, J = 7 Hz), 7.2-7.5 (m, 5H).

*Anal. Calcd. for C<sub>13</sub>H<sub>17</sub>NO<sub>3</sub>S:* C, 58.41; H, 6.41; N, 5.24. Found: C, 58.35; H, 6.68; N, 5.17.

#### $\alpha$ -(Ethoxycarbonylmethylsulfinyl)-*N*-methylaniline (**13**).

By the same procedure as described above for the preparation of the sulfoxides **3a-d**, **7** and **10** the compounds **12** (267 mg, 1 mmole) was oxidized with sodium metaperiodate (214 mg, 1 mmole) to give the sulfoxides **13** (272 mg, 96%), mp 73.5-74.0° (from *n*-hexane); ir (chloroform): 1730, 1640, 1060, 1040 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.25 (t, 3H, J = 7 Hz), 3.30 (s, 3H), 3.63, 3.96 (AB q, 2H, J = 14 Hz), 3.77, 4.12 (AB q, 2H, J = 14 Hz), 4.20 (q, 2H, J = 7 Hz), 7.1-7.6 (m, 5H).

*Anal. Calcd. for C<sub>13</sub>H<sub>17</sub>NO<sub>4</sub>S:* C, 55.11; H, 6.05; N, 4.94. Found: C, 54.86; H, 6.00; N, 5.11.

#### 3-(Ethoxycarbonylmethylthio)-1-methyloxindole (**14**).

By the same procedure (Method B) as described above for the preparation of **4a-d**, **5b,c** or **11**, the sulfoxides **13** (283 mg, 1 mmole) was treated with anhydrous *p*-toluenesulfonic acid (244 mg, 2 mmoles) to give **14** (159 mg, 60%); ir (chloroform): 1730, 1715 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform):  $\delta$  1.26 (t, 3H, J = 7 Hz), 3.20 (s, 3H), 3.30, 3.75 (AB q, 2H, J = 16 Hz), 4.13 (q, 2H, J = 7 Hz), 4.52 (s, 1H), 6.5-7.5 (m, 4H).

*Anal. Calcd. for C<sub>13</sub>H<sub>15</sub>NO<sub>3</sub>S:* C, 58.85; H, 5.70; N, 5.26. Found: C, 59.10; H, 5.66; N, 5.29.

#### 1-Methyloxindole (**15**).

Compound **14** (133 mg, 0.5 mmole) was heated under reflux in ethanol (10 ml) containing Raney nickel (2 g) for 2 hours. The Raney nickel was removed by filtration and the solvent was evaporated off. The residue was recrystallized from ethanol to give **15** (59 mg, 80%), mp 84-85°, lit [6] mp 83.0-84.5°.

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