Some Sulfur-containing Quinoxalines (1)

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A series of quinoxalines having oxygen, chlorine or sulfur substituted at the 2-position and long-chain alkyl, alkylthio, arylthio, alkylthioalkyl or arylthioalkyl groups at the 3-position have been synthesized.

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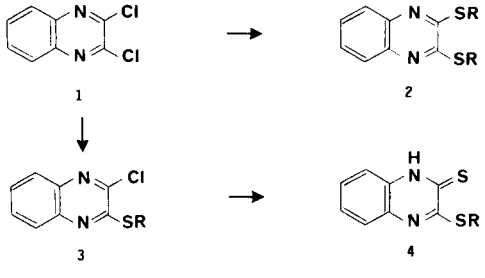
Quinoxaline derivatives have had a variety of uses, such as colormetric agents for the detection and quantitative estimation of metals (2,3), as bacteriocides and dyes (4) and even as heat-stable oil additives (5). In connection with another problem, we were interested in oil-soluble quinoxalines containing sulfur, either on the quinoxaline ring or in certain side chains. We report here the synthesis of properites of some quinoxalines of this type.

Nucleophilic displacement of chloride from 2,3-dichloroquinoxaline (**1**) occurs readily, and this reagent is easily prepared from 2,3-dihydroxyquinoxaline (6). Morrison and Furst (7) prepared 2,3-diethylthioquinoxaline (**2**, R = C_2H_5) in excellent yield from **1** and excess sodium ethyl mercaptide in ethanol (scheme I). Landquist and Silk obtained **2c** (R = *p*-tolyl) by heating **1** and *p*-toluenethiol neat. In preparing the compounds **2a-d** (scheme I), we found that when ethanol was used as a solvent, with just two equivalents of thiol to one of **1**, the product was always contaminated with 2,3-diethoxyquinoxaline. The use of *t*-butyl alcohol as a solvent greatly improved the yields in this displacement, using two equivalents of sodium mercaptide to one of **1**.

It is possible to selectively displace one chloride from **1**, as shown by Newbold and Spring (8), who prepared 2-chloro-3-ethoxyquinoxaline in high yield by reacting one equivalent of sodium ethoxide with **1** in ethanol. Similar reactions using sodium mercaptides in *t*-butyl alcohol gave the 2-chloro-3-alkylthio- or 3-arylthioquinoxalines **3a-d** (scheme I). Dropwise addition of the mercaptide solution to a refluxing solution of **1** in *t*-butyl alcohol decreased the amount of **2** formed as a by-product. The reaction of chloroquinoxalines with thiourea produces isothiuronium salt, which on hydrolysis yields the quinoxaline-2-thiones (9). In some cases, hydrolysis occurs spontaneously in alcoholic solution to yield the thione directly (7), otherwise the intermediate salt was collected and hydrolyzed in aqueous base. The compounds **4a-d** (Scheme I) were prepared in good yield by this procedure.

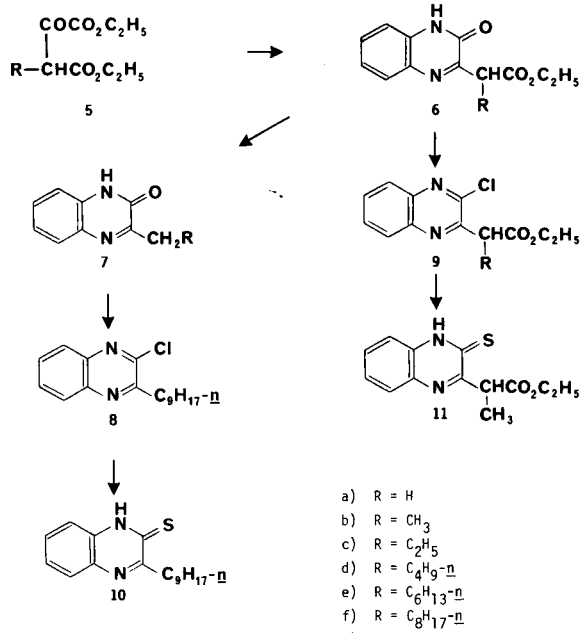
The most convenient procedure for preparing quinoxalones having various alkyl side chains at position 3 (**7**, scheme II) involved condensation of α-ethoxalyl esters (**5**) with *o*-phenylenediamine to produce the quinoxalones (**6**), which on hydrolysis spontaneously decarboxylate to give the desired compounds **7** (10). The required α-ethoxalyl esters (**5**) were readily prepared by allowing the appropriate ester of an aliphatic acid or sulfur-substituted aliphatic acid to form a sodium enolate, and then react with diethyl oxalate (11). Compounds **5a-f** (scheme II) have previously been reported (11). The previously

SCHEME I



a) R = C_4H_9-n, b) R = C_8H_{17}-n, c) R = p-$CH_3C_6H_4$, d) R = p-$CH_3OC_6H_4$.

SCHEME 2



a) R = H
b) R = CH_3
c) R = C_2H_5
d) R = C_4H_9-n
e) R = C_6H_{13}-n
f) R = C_8H_{17}-n
g) R = n-C_4H_9S
h) R = n-$C_4H_9SCH_2CH_2$
i) R = p-$CH_3C_6H_4S$-
j) R = p-$CH_3C_6H_4SCH_2$-
k) R = p-$CH_3C_6H_4S(CH_2)_2$-

unreported oxalyl esters **5g-k** are described in the experimental, but were not distilled, as they decomposed on heating (12). The crude esters could be condensed directly with *o*-phenylenediamine to produce the quinoxalones **6** in good yield. Alkaline hydrolysis followed by acidification produced the quinoxalones **7**, having an alkyl or sulfur-containing side chain at position 3.

A series of 3-substituted-2-quinoxalones (**7**) have been converted to the corresponding 3-substituted-2-chloroquinoxalines (**8**) by treatment with phosphorus oxychloride (13). The 3-nonyl derivative **7f** was converted to the chloro derivative **8**, and this compound converted to the thione **9** in good yield. We have found that the quinoxalones having an ester function present, *e.g.* **6**, can also be converted to the chloroquinoxalines **9** in good yield by treatment with phosphorus oxychloride, using the procedure of Gowenlock, Newbold and Spring (14). One of these (**9b**) was also converted to the thione **11** by with thiourea; the intermediate isothiuronium salt spontaneously hydrolyzing in ethanol solution.

Cheeseman (15) has discussed the structure of 2-hydroxy and 2-mercaptoquinoxalines, and concludes from spectral evidence that these types of compounds are largely in the amide and thioamide forms. The spectral properties of the new derivatives reported here are consistent with this interpretation, and we have therefore indicated the major structural forms of **6, 7, 10** and **11** in scheme II, and used proper nomenclature for these structures.

EXPERIMENTAL

Melting point were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137-B infrared spectrophotometer using potassium bromide pellets unless stated otherwise. Nuclear magnetic resonance spectra were determined on a Varian Model T60 spectrophotometer using tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained on a Varian CH7 mass spectrometer or on a Hewlett-Packard Model 5992A GC/MS mass spectrometer. Elemental analyses were performed at Midwest Micro Labs Inc., Indianapolis, Indiana, and at Canadian Microlab, Vancouver, British Columbia.

General Procedure for the Preparation of 2,3-Dialkylthioquinoxalines (**2**).

To a mixture of two equivalents of thiol in *t*-butyl alcohol was added two equivalents of sodium metal protionwise. The reaction mixture was heated to reflux until all the sodium metal had dissolved. One equivalent of 2,3-dichloroquinoxaline, **1**, (6) was added to the hot reaction mixture portionwise (an exothermic reaction took place). When addition was complete, the contents were heated to reflux for 4 hours, then allowed to cool to room temperature and diluted with water. The aqueous solution was extracted wth methylene chloride, washed with water (2x), dried (magnesium sulfate), filtered and the solvent removed on a rotary evaporator. Trace solvent was removed on a vacuum pump and the crude product purified by recrystallization or distillation.

2,3-Di-*n*-butylthioquinoxaline (**2a**).

This compound was prepared in 88% yield from 73.4 g (0.816 mole) of 1-butanethiol, 18.76 g (0.816 mole) of sodium metal and 80.9 g (0.408 mole) of **1**, bp 180°/0.2 torr (kugelrohr); ir (neat): 3050, 2948-2800, 1608, 1552, 1500, 1480 cm^{-1}; nmr (carbon tetrachloride): δ 0.8-1.17 (t, 6H), 1.33-2.07 (m, 8H), 3.17-3.47 (m, 4H), 7.27-7.83 (m, 4H).

Anal. Calcd. for $C_{16}H_{22}N_2S_2$: C, 62.74; H, 7.19; N, 9.15; S, 20.91. Found: C, 62.44; H, 7.23; N, 9.37; S, 21.01.

2,3-Di-*n*-octylthioquinoxaline (**2b**).

This compound was prepared in 76% yield from 920 mg (6.30 mmoles) of 1-octanethiol, 146 mg (6.35 mmoles) of sodium metal and 623 mg (3.15 mmoles) of **1** in 25 ml of *t*-butyl alcohol, bp 235°/0.2 torr (kugelrohr); ir (neat): 3010, 2900-2740, 1605, 1550, 1495, 1464 cm^{-1}; nmr (carbon tetrachloride): δ 0.72-2.02 (broad, 30H), 3.12-3.45 (t, 4H), 7.28-7.85 (m, 4H).

Anal. Calcd. for $C_{24}H_{38}N_2S_2$: C, 68.90; H, 9.09; N, 6.70. Found: C, 68.79; H, 9.34; N, 6.60.

2,3-Di(*p*-tolylthio)quinoxaline (**2c**).

This compound was prepared in 87% yield from 2.95 g (23.8 mmoles) of *p*-thiocresol, 550 mg (23.8 mmoles) of sodium metal and 2,35 g (11.9 mmoles) of **1** in 25 ml of *t*-butyl alcohol, mp (ethanol) 142-143° (lit (16) mp 140-142°); ir (chloroform): 3038, 2893, 1611, 1505, 1470 cm^{-1}; nmr (deuteriochloroform): δ 2.37 (s, 6H), 7.07-7.67 (m, 12H).

Anal. Calcd. for $C_{22}H_{18}N_2S_2$: C, 70.58; H, 4.81; N, 7.49. Found: C, 70.65; H, 4.98; N, 7.48.

2,3-Di(*p*-methoxyphenylthio)quinoxaline (**2d**).

This compound was prepared in 77% yield from 770 mg (5.5 mmoles) of *p*-methoxybenzenethiol, 161 mg (7 mmoles) of sodium metal and 545 mg (2.75 mmoles) of **1** in 25 ml of *t*-butyl alcohol, mp 160-161° (DMF/ethanol); ir (chloroform), 3000, 2872, 1610, 1560, 1500, 1468 cm^{-1}; nmr (deuteriochloroform): δ 3.87 (s, 6H), 6.85-7.65 (m, 12H).

Anal. Calcd. for $C_{22}H_{18}N_2O_2S_2$: C, 65.00; H, 4.46; N, 6.89. Found: C, 64.70; H, 4.41; N, 6.91.

General Procedure for the Preparation of 2-Chloro-3-alkylthioquinoxalines (**3**).

To a round bottom flask equipped with a condenser and a magnetic stirrer was added one equivalent of thiol in *t*-butyl alcohol. One equivalent of sodium metal was added to the mixture portionwise and the contents heated until all the sodium metal had reacted. The hot reaction mixture (the solution must be hot to remain fluid) was added in portions to a suspension of 2,3-dichloroquinoxaline (**1**) in *t*-butyl alcohol at such a rate as to maintain a gentle reflux. When addition was complete, refluxing was continued for 3 hours. On cooling to room temperature, the mixture was quenched with water and extracted with methylene chloride. The methylene chloride solution was washed with saturated ammonium chloride (2x), dried (magnesium sulfate), treated with activated charcoal, filtered through celite and the solvent removed on a rotary evaporator. Trace solvent was removed on a vacuum pump and the crude product purified by recrystallization or distillation.

2-Chloro-3-butylthioquinoxaline (**3a**).

This compound was prepared in 84% yield from 1.33 g (14.78 mmoles) of 1-butanethiol, 25 ml of *t*-butyl alcohol, 500 mg (21.74 mmoles) of sodium metal and 2.92 g (14.78 mmoles) of **1**, bp 165°/0.2 torr; nmr (carbon tetrachloride): δ 0.80-1.97 (m, 7H), 3.23 (t, 2H), 7.37-7.95 (m, 4H); ms: m/e (relative intensity) 254 (5, M^{+2}), 253 (2.4, M^{+1}), 252 (14.6, M^{+}), 217 (50), 210 (63), 196 (100), 161 (60), 160 (53), 134 (49), 102 (72). This compound was converted to the thio derivative **4a** for analysis.

2-Chloro-3-octylthioquinoxaline (**3b**).

This compound was prepared in 78% yield from 1.48 g (10.1 mmoles) of 1-octanethiol, 235 m (10.2 mmoles) of sodium metal and 2 g (10.1 mmoles) of **1** in 25 ml of *t*-butyl alcohol. A sample was purified by chromatography (silica/90:10, hexane:ether), mp 45-46°; ir (chloroform): 3000, 2900-2740, 1610, 1545, 1498, 1452 cm^{-1}; nmr (deuteriochloroform): δ 0.73-2.10 (m, 15H), 3.10-3.47 (t, 2H), 7.48-8.07 (m, 4H). The compound was converted to **4b** for analysis.

2-chloro-3-*p*-tolythioquinoxaline (**3c**).

This compound was prepared in 70% yield from 1.16 g (11.77 mmoles) of *p*-thiocresol, 345 m (15 mmoles) of sodium metal and 2.33 g (11.77 mmoles) of **1** in 25 ml of *t*-butyl alcohol, mp (ethanol) 120-122°; nmr (deuteriochloroform): δ 2.40 (s, 3H), 7.07-8.07 (m, 8H). This compound was converted to the corresponding thione **4c** for analysis.

2-Chloro-3-(*p*-methoxyphenylthio)quinoxaline (**3d**).

This compound was prepared in 89% yield from 1 g (7.14 mmoles) of *p*-methoxybenzenethiol, 25 ml of *t*-butyl alcohol, 200 mg (8.7 mmoles) of sodium metal and 1.41 gm (7.14 mmoles) of **1**, mp (ethanol) 152-154°; nmr (deuteriochloroform): δ 3.85 (s, 3H), 6.85-7.73 (m, 8H). This compound was converted to the corresponding thione **4d** for analysis.

General Procedure for the Preparation of 3-Alkylthio-2-quinoxaline thiones (**4**).

A mixture of one equivalent of 2-chloro-3-alkylthioquinoxaline (**3**) and 1.5 equivalent of thiourea was heated to reflux in absolute ethanol for 3 hours. The reaction mixture was allowed to cool to room temperature and excess solvent removed on a rotary evaporator. The crude thiuronium salt was combined with aqueous sodium hydroxide and the mixture heated to reflux for 1 hour, cooled to room temperature and made acidic by slow addition of glacial acetic acid. The resulting yellow precipitate was collected, washed with water and dried under vacuum. The crude product was purified by recrystallization unless otherwise noted.

3-Butylthio-2-quinoxalthione (**4a**).

This compound was prepared in 99% yield from 540 mg (2.13 mmoles) of **3a** and 324 mg (4.5 mmoles) of thiourea in 25 ml of absolute ethanol, mp (ethanol) 173-174.5°; ir (chloroform): 3100, 2960-2900, 1620, 1506, 1478, 1350 cm^{-1}; nmr (deuteriochloroform): δ 0.83-1.83 (m, 7H), 3.20 (t, 2H), 7.30-7.93 (m, 4H).

Anal. Calcd. for $C_{12}H_{14}N_2S_2$: C, 57.56; H, 5.64; 11.19. Found: C, 57.78; H, 5.86; N, 10.99.

3-Octylthio-2-quinoxalthione (**4b**).

This compound was prepared in 99% yield from 1 g (3.25 mmoles) of **3b** and 649 mg (8.54 mmoles) of thioures in 20 ml of absolute ethanol. An analytical sample was purified by chromatography (silica/80:20, hexane:ether), mp 128-139°; ir (chloroform): 3000, 2900-2800, 1595, 1550, 1498, 1460, 1385; nmr (deuteriochloroform): 0.80-2.07 (m, 15H), 3.03-3.37 (m, 2H), 7.27-7.90 (m, 4H).

Anal. Calcd. for $C_{16}H_{22}N_2S_2$: C, 62.70; H, 7.24; N, 9.14; S, 20.92. Found; C, 62.54; H, 7.02; N, 9.20; S, 20.75.

3-(*p*-Toylthio)-2-quinoxalthione (**4c**).

This compound was prepared in 42% yield from 500 mg (1.74 mmoles) of **3c** and 200 mg (2.63 mmoles) of thiourea in 25 ml of absolute ethanol, mp (ethanol) 244-245°; ir (chloroform): 3050, 2900-2880, 1600, 1495, 1460, 1322; nmr (hexadeuterioacetone): δ 2.42 (s, 3H), 7.13-7.63 (m, 8H).

Anal. Calcd. for $C_{15}H_{12}N_2S_2$: N, 9.85. Found: N, 9.69.

3-(*p*-Methoxyphenylthio)-2-quinoxalthione (**4d**).

This compound was prepared in 80% yield from 480 mg (1.59 mmoles) of **3d** and 181 mg (2.38 mmoles) of thiourea in 25 ml of absolute ethanol, mp (ethanol) 229°; ir (chloroform): 3050, 2880, 1605, 1555, 1505, 1475, 1400; nmr (hexadeuterioacetone): δ 3.87 (s, 3H), 7.25-7.60 (m, 8H).

Anal. Calcd. for $C_{15}H_{12}N_2OS_2$: C, 59.97; H, 4.03; N, 9.33. Found: C, 59.70; H, 4.10; N, 9.39.

Intermediate Alkyl and Thioalkyl Esters.

Ethyl hexanoate, ethyl octanoate, and ethyl decanoate were prepared from commercially available acids (Aldrich) using the toluene azeotrope method (17).

Ethyl *p*-Tolylthioacetate.

This compound was prepared as previously described (18) from *p*-thiocresol and ethyl chloroacetate in 98% yield, bp 98-100°/1 torr; nmr (carbon tetrachloride): δ 1.07-1.35 (t, 3H, J = 7 Hz), 2.28 (s, 3H), 3.42 (s, 2H), 3.87-4.28 (q, 2H, J = 7 Hz), 6.9-7.02 (q, 4H); ir (neat): 1725 cm^{-1} (CO).

Ethyl *p*-Tolylthiopropionate.

This compound was prepared as previously described (19) from *p*-thiocresol and ethyl acrylate in 83% yield, bp 105°/0.5 torr; nmr (carbon tetrachloride): δ 1.07-1.40 (t, 3H, J = 7 Hz), 2.23-2.62 (m, 5H, including CH_3 singlet at 2.30), 2.87-3.23 (m, 2H), 3.87-4.30 (q, 2H, J = 7 Hz), 6.90-7.30 (q, 4H); ir (neat): 1725 cm^{-1} (CO).

Ethyl 4-*p*-Tolylthiobutyrate.

This compound was prepared by the method of Reppe (20) which required synthesis of the acid from *p*-thiocresol and butyrolactone, followed by esterification to give 93% of a colorless liquid, bp 129°/0.5 torr; nmr (carbon tetrachloride): δ 1.10-1.43 (t, 3H, J = 7 Hz), 1.63-2.18 (m, 2H), 2.23-2.63 (m, 5H, including CH_3 singlet at 2.30), 2.78-3.10 (m, 2H), 3.90-4.33 (q, 2H, J = 7 Hz), 6.93-7.30 (m, 4H); ir (neat): 1716 cm^{-1} (CO).

Ethyl Butanethioacetate.

This compound was prepared as previously described (21) from butanethiol and ethyl chloroacetate in 83% yield, bp 38-39°/0.15 torr; nmr (carbon tetrachloride): δ 0.73-1.77 (m, 10H), 2.47-2.80 (t, 2H), 3.07 (s, 2H), 3.95-4.37 (q, 2H); ir (neat): 1730 cm^{-1} (CO).

Ethyl 4-Butanethiobutyrate.

This compound was prepared by the addition of butanethiol to butyrolactone, followed by esterification of the acid, was obtained in 75% yield, bp 68°/0.2 torr; nmr (carbon tetrachloride): δ 0.75-2.17 (m, 12H), 2.23-2.72 (m, 6H), 3.92-4.35 (q, 2H); ir (neat): 1730 cm^{-1} (CO).

General Procedure for the Preparation of α-Ethoxalyl Esters (**5**).

Following the procedure of Adickes and Andresen (11), one molar equivalent of sodium was dissolved in absolute ethanol, with refluxing to completion. Ethanol was removed by heating under reduced pressure, and the flask containing dry sodium ethoxide purged with dry nitrogen. Anhydrous ether was added, and then one equivalent of diethyl oxalate was slowly added with rapid stirring. The ether began refluxing during this addition. One equivalent of ester was added, and the reaction mixture heated to gentle reflux overnight. The reaction mixture was allowed to cool to room temperature, then quenched with water and the ether layer separated. The ether layer was washed with water, then discarded. The combined aqueous layers were washed (2x) with ether (discarded) (sometimes foaming and emulsions hampered layer separation) then acidified with 3*N* hydrochloric acid. The precipitate was extracted with ether (3x), and the combined ether layers washed with water, then saturated ammonium chloride. The solution was dried (magnesium sulfate), treated with activated charcoal, filtered through celite and the solvent removed on a rotary evaporator. The residueal liquid was warmed under reduced pressure ot remove traces of solvent. The crude products were pale yellow in color. These crude esters were used directly in the next step. The diesters **5a-f**, where R = H methyl, ethyl, *n*-butyl and *n*-octyl, were obtained in yield of 48-64% by this method (11).

Ethyl 2-Ethoxalylbutanethioacetate (**5g**).

This compound was prepared in 82% yield from 782 mg (34 mmoles) of sodium metal, 4.97 g (34 mmoles) of ethyl oxalate and 6 g (34 mmoles) of ethyl butanethioacetate; nmr (carbon tetrachloride): δ 0.63-1.75 (m, 13H, including $-CH_3$ triplet centered at 1.38, J = 7 Hz), 2.43-2.78 (m, 2H), 4.05-4.65 (m, 5H); ir (thin film): 1725 cm^{-1} (broad, C=O).

Ethyl 2-ethoxalyl-4-butanethiobutyrate (**5h**).

This compound was prepared in 72% yield from 902 mg (39.2 mmoles) of sodium metal, 5.73 g (39.2 mmoles) of ethyl oxalate and 8 g (39.2 mmoles) of ethyl 4-butanethiobutyrate; nmr (carbon tetrachloride): δ 0.78-1.68 (m, 15H), 1.90-2.68 (m, 4H), 3.95-4.48 (m, 5H); ir (thin film): 1720 cm^{-1} (broad, C=O).

Ethyl 2-Ethoxalyl-*p*-tolylthioacetate (**5i**).

This compound was prepared in 83% yield from 2.75 g (0.12 mole) of sodium metal, 17.46 g (0.12 mole) of ethyl oxalate and 25 g (0.119 mole) of ethyl *p*-tolylthioacetate; nmr (carbon tetrachloride): δ 1.03-1.50 (m, 6H, overlapping $-CH_3$ triplet centered at 1.20 and 1.30, J = 7 Hz), 2.30 (s, 3H), 3.98-4.52 (m, 4H, overlapping $-CH_2-$ quartets, J = 7 Hz), 6.87-7.33 (m, 4H); ir (thin film): 1740 cm^{-1} (C=O).

Ethyl 2-Ethoxalyl-3-*p*-tolylthiopropionate (**5j**).

This compound was prepared in 43% yield from 2 g (87 mmoles) of sodium metal, 12.41 g (85 mmoles) of ethyl oxalate and 18.57 g (82.9 mmoles) of ethyl 3-*p*-tolylthiopropionate; nmr (carbon tetrachloride): δ 1.00-1.53 (m, 6H), 2.27 (s, 3H), 3.22, 3.33 and 3.83-4.43 (m, 7H), 6.83-7.33 (m, 4H); ir (thin film): 1725 cm^{-1} (C=O).

Ethyl 2-Ethoxalyl-4-*p*-tolylthiobutyrate (**5k**).

This compound was prepared in 76% yield from 1.22 g (53.23 mmoles) of sodium metal, 7.77 g (53.23 mmoles) of ethyl oxalate and 12.67 g (53.23 mmoles) of ethyl 4-*p*-tolylthiobutyrate; nmr (carbon tetrachloride): δ 1.06-1.48 (m, 6H, overlapping $-CH_3$ triplets centered at 1.18 and 1.30, J = 7 Hz), 1.90-2.37 (m, 5H, overlapping $-CH_3$ singlet t 2.25 and $-CH_2-$ quartet), 2.65-3.07 (t, 2H), 3.92-4.47 (m, 5H), 6.85-7.32 (m, 4H); ir (thin film): 1730 cm^{-1} (broad, C=O).

General Procedure for the Preparation of Ethyl α-(2-oxo-3-quinoxalyl) esters (**6**).

Following the method of L'Italien and Banks (10), one equivalent of *o*-phenylenediamine was dissolved in a minimum amount of 95% ethanol heated on a steam bath. One equivalent of the appropriate α-ethoxlyl ester diluted with a small amount of ethanol was added and heating continued for about 15 minutes. Water was then slowly added to the hot solution until it became cloudy. The mixture was allowed to cool to room temperature, then refrigerated, and the resulting yellow crystals or solid (in some cases, the product oiled out and solidified as a cake) collected by filtration and washed with water. The crude product was purified by recrystallization unless otherwise noted.

Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)acetate (**6a**).

This compound was prepared in 64% yield from 3.88 g (35.9 mmoles) of *o*-phenylenediamine and 6.75 g (35.9 mmoles) of ethyl 2-ethoxalylacetate in 50 ml of ethanol, mp (methanol/water) 206-209° (lit (22) mp 210°).

Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)propionate (**6b**).

This compound was prepared in 84% yield from 18.85 g (0.175 mole) of *o*-phenylenediamine and 35.26 g (0.175 mole) of ethyl 2-ethoxalylpropionate; mp (crude) 161-163° (lit (10) mp 160-162°).

Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)butyrate (**6c**).

This compound was prepared in 88% yield from 7.32 g (67.82 mmoles) of *o*-phenylenediamine and 14.65 g (67.82 mmoles) of ethyl 2-ethoxalylbutyrate, mp (ethanol) 112-113.5°; nmr (deuteriochloroform): δ 0.90-1.40 (m, 6H, two methyl triplets centered at 1.07 and 1.23, J = 7 Hz), 1.93-2.50 (p, 2H, J = 7 Hz), 3.98-4.42 (q, 3H, J = 7 Hz), 7.13-8.00 (m, 4H), 12.40-12.86 (broad, 1H).

Anal. Calcd. for $C_{14}H_{16}N_2O_3$: C, 64.61; H, 6.15; N, 10.77. Found: C, 64.96; H, 6.20; N, 10.53.

Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)hexanoate (**6d**).

This compound was prepared in 80% yield from 5.08 g (47.01 mmoles) of *o*-phenylenediamine and 11.48 g (47.01 mmoles) of ethyl 2-ethoxalylhexanoate in 20 ml of ethanol, mp (ethanol/water) 136-137°; ir (chloroform): 3198 (NH), 2960 (ArH), 2880-2790 (CH), 1725 (ester CO), 1665 (amide CO), 1600, 1555, 1500, 1470 (ArC-C, C-N) cm^{-1}; nmr (deuteriochlorofrom): δ 0.70-1.67 (m, 8H, including -CH_3 triplet centered at 1.25), 1.93-2.43 (m, 2H), 4.00-4.43 (m, 3H, overlapping quartet and triplet), 7.17-8.00 (m, 4H), 11.40-12.87 (broad, 1H).

Anal. Calcd. for $C_{16}H_{20}N_2O_3$: C, 66.67; H, 6.94; N, 9.72. Found: C, 66.65; H, 6.95; N, 9.79.

Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)octanoate (**6e**).

This compound was prepared in 81% yield from 2 g (18.5 mmoles) of *o*-phenylenediamine and 5 g (18.38 mmoles) of ethyl 2-ethoxalyloctanoate in 10 ml of ethanol, mp (ethanol/water) 103-104°; ir (chloroform): 3160 (NH), 3000 (ArH), 2920-2800 (CH), 1725 (ester CO), 1660 (amide CO), 1608, 1570, 1492, 1468 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 0.70-1.67 (m, 14H), 1.93-2.37 (m, 2H), 4.00-4.40 (m, 3H, overlapping triplet and quartet), 7.13-7.95 (m, 4H), 12.60-12.93 (broad, 1H).

Anal. Calcd. for $C_{18}H_{24}N_2O_3$: C, 68.33; H, 7.65; N, 8.86. Found: C, 68.88; H, 7.88; N, 8.99.

Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)decanoate (**6f**).

This compound was prepared in 91% yield from 1.8 g (16.67 mmoles) of *o*-phenylenediamine and 5 g (16.67 mmoles) of ethyl 2-ethoxalyldecanoate in 20 ml of ethanol, mp (ethanol/water) 98-99°; ir (chloroform): 3155 (NH), 2900 (ArH), 2860-2700 (CH), 1725 (ester CO), 1660 (amide CO), 1600, 1545, 1490, (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 0.67-1.67 (m, 18H), 1.80-2.43 (m, 2H), 4.03-4.43 (m, 3H), 7.20-8.00 (m, 4H), 12.63-12.87 (broad, 1H).

Anal. Calcd. for $C_{20}H_{28}N_2O_3$: C, 69.76; H, 8.14; N, 8.14. Found: C, 69.92; H, 8.39; N, 8.17.

Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)butanethioacetate, (**6g**).

This compound was prepared in 90% yield from 783 mg (7.25 mmoles) of *o*-phenylenediamine and 2 g (7.24 mmoles) of ethyl 2-ethoxalylbutanethioacetate, mp (ethanol 103-104°; ir (chloroform): 3280, 3180 (NH), 2950 (ArH), 2900-2780 (CH), 1725 (ester CO), 1650 (amide CO), 1590, 1560, 1510, 1450 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 0.70-1.83 (m, 10H, including $-CH_3$ triplet at 1.27, J = 7 Hz), 2.63-2.97 (t, 2H, J = 7 Hz), 4.07-4.47 (q, 2H, J = 7 Hz), 5.03 (s, 1H), 7.13-8.00 (m, 4H), 12.27-13.03 (broad, 1H).

Anal. Calcd. for $C_{16}H_{20}N_2O_3S$: C, 59.97; H, 6.29; N, 8.75. Found: C, 59.73; H, 6.29; N, 8.65.

Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)-4-butanethiobutyrate, (**6h**).

This compound was prepared in 71% yield from 1.8 g (16.7 mmoles) of *o*-phenylenediamine and 5 g (16.44 mmoles) of ethyl 2-ethoxalyl-4-butane thiobutyrate in 25 ml of ethanol mp (ethanol) 85-86.5°; ir (chloroform); 3200, (NH), 3010 (ArH), 2930-2810 (CH), 1725 (ester CO), 1660 (amide CO), 1620, 1506, 1485 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 0.70-1.77 (m, 10H, including $-CH_3$ triplet at 1.22, J = 7 Hz), 2.37-2.93 (m, 6H), 4.02-4.60 (m, 3H, overlapping triplet and quartet, J = 7 Hz), 7.12-7.98 (m, 4H), 12.40-12.93 (broad, 1H).

Anal. Calcd. for $C_{18}H_{24}N_2O_3S$: C, 62.02; H, 6.94; N, 8.04. Found: C, 62.33; H, 7.28; N, 8.18.

Ethyl α-(Oxo-1*H*-3-quinoxalyl)-*p*-tolylthioacetate (**6i**).

This compound was prepared in 51% yield from 2.93 g (27.12 mmoles) of *o*-phenylenediamine and 8.41 g (27.12 mmoles) of ethyl 2-ethoxalyl-*p*-tolylthioacetate, mp 125-126.5°; ir (chloroform): 3195 (NH), 3005 (ArH), 2900-2800 (CH), 1730 (ester CO), 1660 (amide CO), 1610, 1565, 1500, 1472 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 1.07-1.30 (t, 3H, J = 7 Hz), 2.67 (s, 3H), 4.03-4.38 (q, 2H, J = 7 Hz), 5.33 (s, 1H), 6.95-7.75 (m, 8H), 12.68-12.98 (broad, 1H).

Anal. Calcd. for $C_{19}H_{18}N_2O_3S$: C, 64.40; H, 5.08; N, 7.91. Found: C, 64.57; H, 5.23; N, 7.77.

Ethyl α-(2-Oxo-3-1*H*-quinoxalyl)-3-*p*-tolylthiopropionate, (**6j**).

This compound was prepared in 79% yield from 1.67 g (15.43 mmoles) of *o*-phenylenediamine and 5 g (15.43 mmoles) of ethyl 2-ethoxalyl-3-*p*-tolylthiopropionate in 25 ml of ethanol, mp (ethanol) 141-142°: ir (chloroform): 3220 (NH), 3010 (ArH), 2950-2900 (CH), 1725 (ester CO), 1660 (amide CO), 1600, 1545, 1490 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 1.22 (t, 3H, J = 7 Hz), 2.23 (s, 3H), 3.65-3.92 (dd, 2H, J = 7 Hz), 4.02-4.72 (m, 3H, overlapping triplet and quartet, J = 7 Hz), 6.82-7.98 (m, 8H), 12.35-12.85 (broad, 1H).

Anal. Calcd. for $C_{20}H_{20}N_2O_3S$: C, 65.19; H, 5.47; N, 7.60. Found: C, 65.18; H, 5.55; N, 7.42.

Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)-4-*p*-tolylthiobutyrate, (**6k**).

This compound was prepared in 43% yield from 1.6 g (14.8 mmoles) of *o*-phenylenediamine and 5 g (14.79 mmoles) of ethyl 2-ethoxalyl-4-*p*-tolylthiobutyrate, mp 128-130°; ir (chloroform): 3200 (NH), 3000 (ArH), 2920-2820 (CH), 1720 (ester CO), 1660 (amide CO), 1610, 1550, 1480, 1465 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 1.08-1.40 (t, 3H, J = 7 Hz), 2.23-2.73 (m, 5H, including $-CH_3$ singlet at 2.27), 2.83-3.27 (q, 2H, J = 7 Hz), 4.03-4.62 (m, 3H, overlapping quartet and triplet, J = 7 Hz), 6.93-7.98 (m, 8H), 12.33-12.65 (broad, 1H).

Anal. Calcd. for $C_{21}H_{22}N_2O_3S$: C, 65.97; H, 5.76; N, 7.33; S, 8.38. Found: C, 65.89; H, 5.80; N, 7.07; S, 8.21.

General Procedure for the Preparation of 3-Substituted-2-quinoxalones (**7**) from Ethyl α-(2-Oxo-1*H*-3-quinoxalyl)esters (**6**).

The appropriate α-(2-Oxo-1*H*-3-quinoxalyl)ester was suspended in an aqueous solution of sodium hydroxide, and heated to reflux for 1 hour with concommittant dissolution of the solid material. The solution was allowed to cool to room temperature then made acidic by slow addition of 3*N* hydrochloric acid, causing carbon dioxide evolution and precipitation of a white solid. The mixture was slowly heated to reflux for 1 hour, allowed to cool to room temperature, further cooled in an ice bath and the solid collected. The crude product was washed with water and dried under vacuum to yield 3-substituted 2-quinoxalones. The crude material was further purified by dissolution in dilute sodium hydroxide, treated with Norite and re-precipitation with glacial acetic acid unless otherwise noted.

3-Nonyl-2-quinoxalone (**7f**).

This compound was prepared in 86% yield from 400 ml (1.16 mmoles) of **6** (R = *n*-octyl) in 15 ml of 10% sodium hydroxide, mp (methanol/ethanol/water) 128-129° (lit (22) mp 127°).

3-Butanethiomethyl-2-quinoxalone (**7g**).

This compound was prepared in 84% yield from 840 mg (2.625 mmoles) of **6g** in 30 ml of 10% sodium hydroxide. An analytical sample was purified by column chromatography (silica/60:40, methylene chloride:ether), mp 145.5°; ir (chloroform): 3210, 3190 (NH), 3050 (ArH), 2950-2850 (CH), 1660 (amide CO), 1600, 1498, 1470 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 0.77-1.82 (m, 7H), 2.65 (t, 2H), 3.92 (s, 2H), 7.22-7.88 (m, 4H), 12.12-12.53 (broad, 1H).

Anal. Calcd. for $C_{13}H_{16}N_2OS$: N, 11.28. Found: N, 11.00.

3-(3'-Butanethiopropyl)-2-quinoxalone (**7h**).

This compound was prepared in 94% yield from 1.8 g (5.17 mmoles) of **6h** in 30 ml of 5% sodium hydroxide. An analytical sample was purified by chromatography (silica/60:40, methylene chloride:ether), mp 90-91°; ir (chloroform): 3100 (NH), 3040 (ArH), 2950-2820 (CH), 1660 (amide CO), 1610, 1560, 1485 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 0.72-1.07 (m, 3H), 1.20-1.77 (m, 4H), 1.98-2.90 (m, 6H), 2.97-3.30 (t, 2H), 7.23-7.97 (m, 4H), 12.13-12.93 (broad, 1H).

Anal. Calcd. for $C_{15}H_{20}N_2OS$: C, 65.18; H, 7.29; N, 10.14. Found: C, 64.96; H, 7.50; N, 10.40.

3-(*p*-Tolylthiomethyl)-2-quinoxalone (**7i**).

This compound was prepared in 93% yield from 3.11 g (8.78 mmoles) of **6i** in 40 ml of 10% sodium hydroxide. An analytical sample was purified by column chromatography (silica/60:40, methylene chloride:ether); mp 183°; ir (chloroform): 3100 (NH), 3050 (ArH), 3000 (CH), 1660 (amide CO), 1590, 1550, 1472 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 2.27 (s, 3H), 4.33 (s, 2H), 6.92-7.85 (m, 8H), 12.35-12.72 (broad, 1H).

Anal. Calcd. for $C_{16}H_{14}N_2OS$: C, 68.06; H, 5.00; N, 9.92. Found: C, 67.71; H, 5.11; N, 9.83.

3-(3'-*p*-Tolylthiopropyl)-2-quinoxalone (**7k**).

This compound was prepared in 89% yield from 1 g (2.60 mmoles) of **6k** in 50 ml of 10% sodium hydroxide. An analytical sample was purified by chromatography (silica/50:50, methylene chloride:ether), mp 147-148.5°; ir (chloroform): 3200 (NH), 3050 (ArH), 2950-2870 (CH), 1660 (amide CO), 1600, 1547, 1505, 1475 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 2.00-2.45 (m, 5H, including $-CH_3$-singlet at 2.28), 2.98-3.32 (m, 4H), 6.92-7.98 (m, 8H).

Anal. Calcd. for $C_{18}H_{18}N_2OS$: C, 69.68; H, 5.81; N, 9.03. Found: C, 69.89; H, 5.83; N, 9.07.

General Procedure for the Preparation of 3-Substituted 2-Chloroquinoxalines (**8** or **9**).

A mixture of a quinoxalone (**6** or **7**) and excess freshly distilled phoshorus oxychloride was heated on a pre-heated oil bath at 120° for 30 minutes. The mixture was allowed to cool to room temperature and excess phosphorus oxychloride removed under reduced pressure. The residue was diluted with diethyl ether and cautiously poured over a mixture of crushed ice/water. The solution was made basic with ammonium hydroxide and extracted with diethyl ether (3x). The combined ether extracts were washed with saturated ammonium chloride, dried (magnesium sulfate), treated with activated charcoal and filtered through celite. The solvent was removed on a rotory evaporator and the crude product purified by recrystallization.

2-Chloro-3-nonylquinoxaline (**8**).

Prepared in 84% yield from 2.54 g (9.34 mmoles) of **7f** and 20 ml of phosphorus oxychloride, mp 42-43° (lit (13) mp 40-41.5°).

Ethyl α-(2-Chloro-3-quinoxalyl)acetate (**9a**).

Prepared in 65% yield from 500 mg (2.15 mmoles) of **6a** and 5 ml of phosphorus oxychloride, mp (ether/hexane) 81-82°; ir (chloroform): 3050 (ArH), 2980 (CH), 1720 (ester CO), 1600-1450 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 1.13-1.43 (t, 3H, J = 7 Hz), 4.07-4.47 (m, 4H, overlapping $-CH_2-$ singlet at 4.20 and quartet, J = 7 Hz), 7.63-8.20 (m, 4H).

Anal. Calcd. for $C_{12}H_{11}ClN_2O_2$: C, 57.50; H, 4.39; N, 11.18. Found: C, 57.36; H, 4.62; N, 10.82.

Ethyl α-(2-Chloro-3-quinoxalyl)propionate (**9b**).

This compound was prepared in 89% yield from 500 mg (2.03 mmoles) of **6b** and 3 ml of phosphorus oxychloride, mp (ethanol) 46-48°: ir (chloroform): 3000 (ArH), 2960-2900 (CH), 1725 (ester CO), 1605, 1540-1460 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 1.07-1.40 (t, 3H, J = 7 Hz), 1.63-1.90 (d, 3H, J = 7 Hz), 4.00-4.67 (m, 3H, overlapping quartets, J = 7 Hz), 7.70-8.17 (m, 4H).

Anal. Calcd. for $C_{13}H_{13}ClN_2O_2$: C, 58.99; H, 4.92; N, 10.59. Found: C, 58.76; H, 4.99; N, 10.42.

Ethyl α-(2-Chloro-3-quinoxalyl)butyrate (**9c**).

This compound was prepared in 84% yield from 8 g (30.76 mmoles) of **6c** and 50 ml of phosphorus oxychloride, bp 170°/0.2 torr (kugelrohr); ir (neat): 2950-2800 (ArH, CH), 1725 (ester CO), 1605, 1549, 1500, 1470 (ArC-C, C-N) cm^{-1}; nmr (carbon tetrachloride): δ 0.88-1.42 (m, 6H, including $-CH_3$ triplets at 1.05 and 1.22, J = 7 Hz), 1.98-2.53 (q, 2H, J = 7 Hz), 3.95-4.38 (q, 3H, J = 7 Hz), 7.55-8.15 (m, 4H).

Anal. Calcd. for $C_{14}H_{15}ClN_2O_2$: C, 60.32; H, 5.42; N, 10.05. Found: C, 60.62; H, 5.39; N, 9.87.

Ethyl α-(2-Chloro-3-quinoxalyl)hexanoate (**9d**).

This compound was prepared in 83% yield from 1.5 g (5.2 mmoles) of **6d** and 10 ml of phosphorus oxychloride, bp 175°/0.5 torr (kugelrohr); ir (neat): 3010 (ArH), 2930-2850 (CH), 1725 (ester CO), 1600-1500 (ArC-C, C-N) cm^{-1}; nmr (carbon tetrachloride): δ 0.68-1.65 (m, 10H, including $-CH_3$ triplet at 1.17, J = 7 Hz), 2.02-2.50 (m, 2H), 3.98-4.55 (m, 3H, overlapping quartet and triplet, J = 7 Hz), 7.52-8.15 (m, 4H).

Anal. Calcd. for $C_{16}H_{19}ClN_2O_2$: C, 62.64; H, 6.24; N, 9.13. Found: C, 62.84; H, 6.48; N, 9.30.

Ethyl α-(2-Chloro-3-quinoxalyl)octanoate, (**9e**).

This compound was prepared in 85% yield from 2 g (6.33 mmoles) of

6e and 8 ml of phosphorus oxychloride, bp 180°/0.05 torr (kugelrohr); ir (neat): 3000 (ArH), 2950-2850 (CH), 1725 (ester CO), 1610, 1555, 1492 (ArC-C C-N) cm^{-1}; nmr (carbon tetrachloride): δ 0.73-1.67 (m, 14H), 2.00-2.52 (m, 2H), 4.00-4.55 (m, 3H), 7.60-8.22 (m, 4H).

Anal. Calcd. for $C_{18}H_{23}ClN_2O_2$: C, 64.56; H, 6.92; N, 8.37. Found: C, 64.34; H, 7.30; N, 8.38.

Ethyl α-(2-Chloro-3-quinoxalyl)decanoate, (**9f**).

This compound was prepared in 83% yield from 1 g (2.90 mmoles) of **6f** and 8 ml of phosphorus oxychloride, bp 195°/0.05 torr (kugelrohr); ir (neat): 3050 (ArH), 2930-2840 (CH), 1725 (ester CO), 1600-1500 (ArC-C, C-N) cm^{-1}; nmr (carbon tetrachloride): δ 0.55-1.52 (m, 18H), 1.88-2.32 (m, 2H), 3.85-4.35 (m, 3H), 7.38-8.02 (m, 4H).

Anal. Calcd. for $C_{20}H_{27}ClN_2O_2$: C, 66.19; H, 7.50; N, 7.72. Found: C, 66.23; H, 7.76; N, 7.58.

3-Nonylquinoxaline-2-thione (**10**).

A mixture of 41.25 g (0.142 mole) of **8** and 16.2 g (0.213 mole) of thiourea in 400 ml of absolute ethanol was heated to reflux for 2 hours. The mixture was allowed to cool to room temperature and excess solvent removed on a rotary evaporator. To the residue was added 600 ml of 20% sodium hydroxide and the mixture was heated to reflux for 1 hour, allowed to cool to room temperature and make acidic with glacial acetic acid. The resulting yellow precipitate was collected, washed with water and dried under vacuum to yield 40.32 g (99%) of product melting at 140-143°. An analytical sample was recrystallized from ethanol, mp 142-144°; ir (chloroform): 3000 (ArH), 2950-2800 (CH), 1570, 1495, 1450 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 0.67-2.10 (m, 17H), 3.08-3.43 (t, 2H), 7.27-7.97 (m, 4H).

Anal. Calcd. for $C_{17}H_{24}N_2S$: C, 70.78; H, 8.39; N, 9.71; S, 11.11. Found: C, 70.61; H, 8.42; N, 9.91; S, 11.24.

Ethyl α-(2-Thio-3-quinoxalyl)propionate (**11**).

A mixture of 500 mg (1.89 mmoles) of **9b** and 144.4 mg (1.9 mmoles) of thiourea in 10 ml of absolute ethanol was stirred at room temperature for 3 days. The mixture was diluted with water and 5% sodium bicarbonate and extracted with methylene chloride. The organic extracts were dried (magnesium sulfate), treated with activated charcoal and filtered through celite. The solvent was removed on a rotary evaporator and trace solvent removed on a vacuum pump. A yellow oil resulted which later crystallized (370 mg, 75%), mp (ethanol) 125-127°; ir (chloroform): 3000 (ArH), 2900-2820 (CH), 1700 (ester CO), 1600, 1572, 1510 (ArC-C, C-N) cm^{-1}; nmr (deuteriochloroform): δ 1.27 (t, 3H, J = 7 Hz), 1.68 (d, 3H, J = 7 Hz), 4.22 (q, 2H, J = 7 Hz), 4.92 (q, 1H, J = 7 Hz), 7.30-8.00 (m, 4H), 12.33-13.00 (broad, 1H).

Anal. Calcd. for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38; N, 10.68. Found: C, 59.71; H, 5.33; N, 10.82.

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