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Quinazolines and 1,4-Benzodiazepines. 76[1]. Reactions of Some Di-4-morpholinylphosphinyloxy Imines

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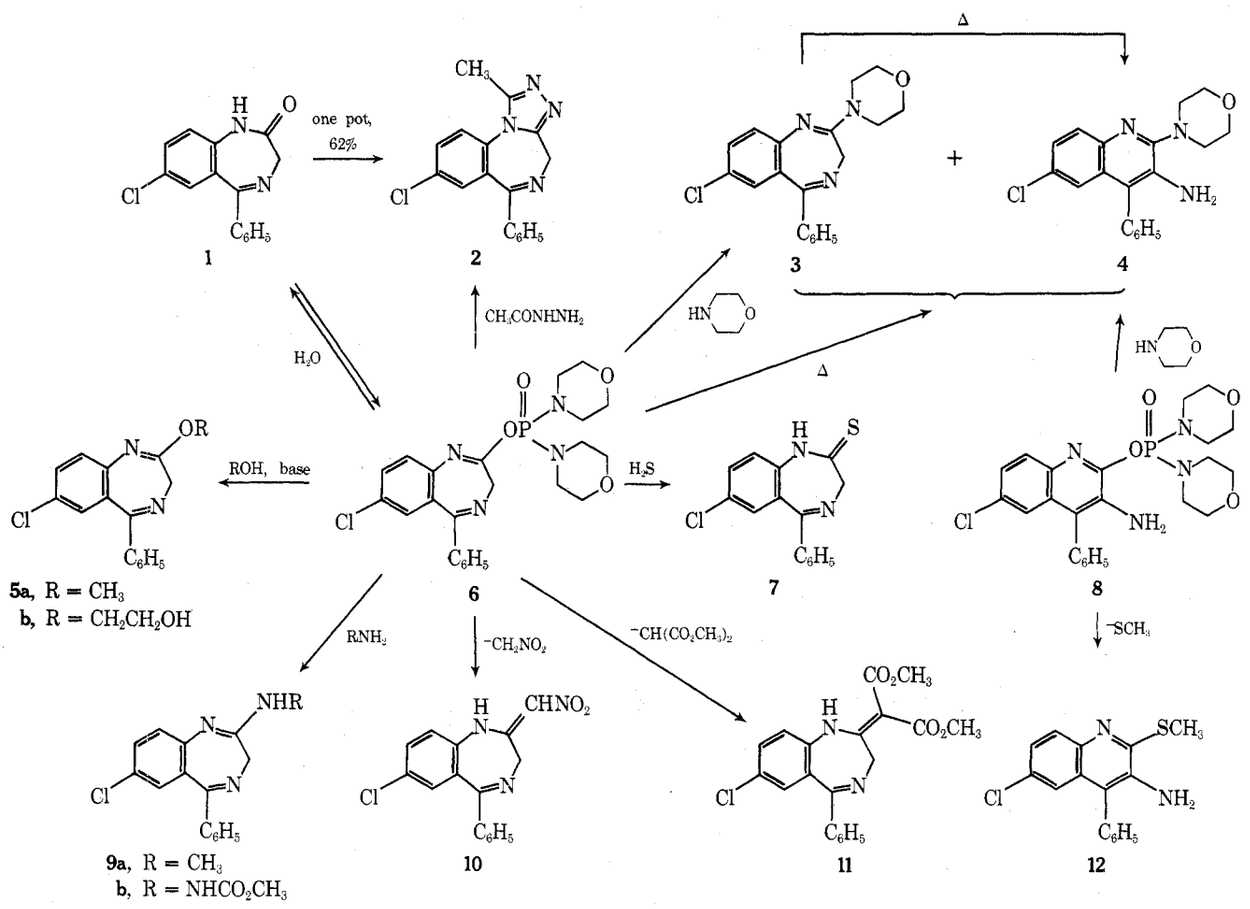
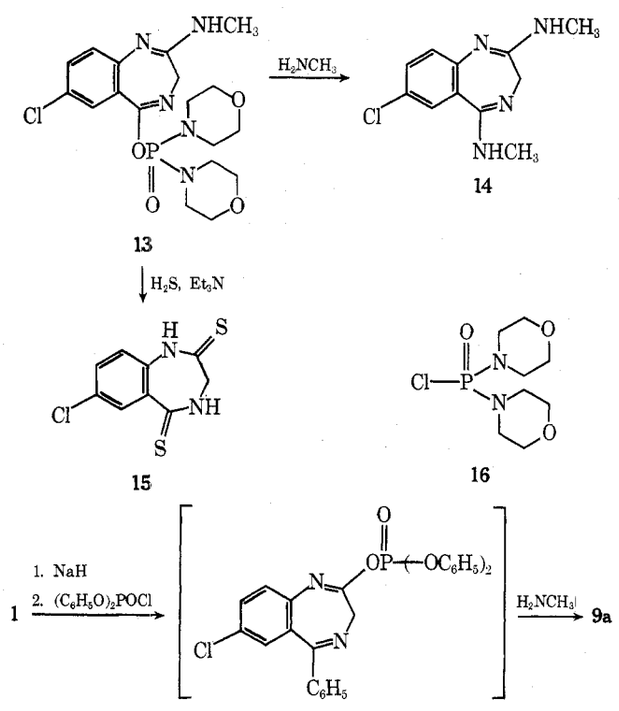
The reaction of 7-chloro-2-(di-4-morpholinyl)phosphinyloxy-5-phenyl-3*H*-1,4-benzodiazepine (**6**), 7-chloro-5-(di-4-morpholinyl)phosphinyloxy-2-methylamino-3*H*-1,4-benzodiazepine (**13**), and 3-amino-6-chloro-2-(di-4-morpholinyl)phosphinyloxy-4-phenylquinoline (**8**) with a variety of nucleophiles illustrates the imidoyl character of the dimorpholinylphosphinyloxy imines. Of particular interest is the facile reaction of **6** with amines, alcohols, hydrogen sulfide, and carbanions to give the corresponding 2-substituted benzodiazepines. Pyrolysis of **6** in refluxing trichlorobenzene afforded a mixture of 7-chloro-2-(4-morpholinyl)-5-phenyl-3*H*-1,4-benzodiazepine (**3**) and 3-amino-6-chloro-2-(4-morpholinyl)-4-phenylquinoline (**4**). Compound **3** under the same conditions was shown to isomerize to **4**.

The chemical activation of secondary amides via transformations to imidates,[2] imidoyl halides,[2] thioamides,[3] amidines,[2c,4] and *N*-nitrosoamidines,[5] among others, have imparted great synthetic utility to these amides as intermediates. We have recently reported that medicinally interesting cyclic secondary amides in the 1,4-benzodiazepine[6] series can be derivatized by O-phosphorylation under *mild, basic* conditions.[7] Phosphorylation of the ambident amide anions with dimorpholinylphosphinic chloride (**16**) afforded the novel dimorpholinylphosphinyloxy imines such as **6** and **13** which were isolated in good yields. In this paper, we describe reactions of some of these dimorpholinylphosphinyloxy imines which point to their versatility as intermediates.[8] These intermediates offer a valuable alternate to other imidoyl compounds which are often difficult to generate in sensitive molecules.

7-Chloro-2-(di-4-morpholinylphosphinyloxy)-5-phenyl-3*H*-1,4-benzodiazepine (**6**)[7] reacts with a variety of nucleophiles to give various 2-substituted benzodiazepines through displacement of the dimorpholinylphosphinyloxy group. Exposure of **6** to methanol containing sodium methoxide and to ethylene glycol containing triethylamine afforded the corresponding 2-alkoxy derivatives **5a** and **5b** in 87 and 82% yields, respectively. The displacement reaction is nearly instantaneous at room temperature with hydrogen sulfide–triethylamine, methylamine, and methyl hydrazinocarboxylate, giving **7** (78%), **9a** (96%), and **9b** (84%), respectively. Of particular interest is the carbon–carbon bond formation through the displacement of the dimorpholinylphosphinyloxy group with carbanions. We have found (conditions not optimized) that the reaction of **6** with the anions of nitromethane and dimethyl malonate afforded 7-chloro-1,3-dihydro-2-nitromethylene-5-phenyl-2*H*-1,4-benzodiazepine (**10,** 27%)[9] and 7-chloro-1,3-dihydro-2-(dimethoxymalonylidene)-5-phenyl-2*H*-1,4-benzodiazepine (**11,** 13%),[5] respectively. The utility of **6** as an intermediate has been further demonstrated by its facile conversion (80%) to 1-methyl-6-phenyl-4*H*-*s*-triazolo[4,3-*a*][1,4]benzodiazepine (**2**),[3c,10] a benzodiazepine of clinical interest.[6] We have also found that compound **2** can be prepared in a simple procedure by reacting 7-chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-one (**1**) with sodium hydride, di-4-morpholinylphosphinic chloride,[7] and acetylhydrazide, in that order, in the same reaction vessel. Compound **2** was readily isolable in 62% yield.

Hydrolysis of **6** (aqueous tetrahydrofuran, room temperature, 7 days) led to lactam **1** (52%) and, interestingly, the 2-morpholinyl derivative **3** as a by-product in 8% yield. When the hydrolysis was conducted in refluxing aqueous tetrahydrofuran, compound **3** was obtained in 21% yield. Higher yield of **3** was obtained when **6** was treated with morpholine (74%). Pyrolysis of **6** in refluxing 1,2,4-trichlorobenzene (214 °C) afforded **3** in 26% yield along with an isomeric product **4** obtained in 17% yield. The assignment of the 3-amino-2-morpholinylquinoline structure **4** was correlated with a synthesis from 3-amino-6-chloro-2-(di-4-morpholinyl)phosphinyloxy-4-phenylquinoline (**8**)[7] and morpholine. The fact that **4** is a secondary pyrolysis product derived from **3** was demonstrated by the conversion of **3** to **4** under similar conditions. The pyrolytic conversion of the di-4-morpholinylphosphinyloxy imine **6** to morpholinylimine **3** is an exemplification of the process proposed in the literature[11] to explain the conversion of secondary amides to their corresponding amidines by heating with amides of phosphoric acid. Although phosphorodiamidates of type **6** have been proposed as intermediates in these reactions, it appears that in no case have they been isolated.





The reaction of **8**, an aromatic dimorpholinylphosphinyloxy imine, with morpholine was quite sluggish compared with the same reaction involving **6**. Since the condition used was vigorous (refluxing morpholine, 46 h, 12% yield), it is not clear if this reaction proceeds via intermolecular or intramolecular displacement. Both types of reaction have been observed in the case of **6**. To show that nucleophilic displacement can occur in the case of **8**, the compound was treated with the anion of methyl mercaptan in refluxing methyl Cellosolve (2 h). The 2-methylthioquinoline derivative **12** was isolated in 26% yield.

A third dimorpholinylphosphinyloxy imine examined was 7-chloro-5-(di-4-morpholinyl)phosphinyloxy-2-methylamino-3*H*-1,4-benzodiazepine (**13**).[7] The reactivity of **13** toward nucleophiles was intermediate that of compound **6** and of compound **8**. Heating was required (steam bath, 24 h) for the complete reaction of **13** with methylamine. The 5-methylamino derivative **14** was obtained in 48% yield. When a solution of **13** in tetrahydrofuran containing triethylamine was saturated with hydrogen sulfide and allowed to stand overnight at room temperature, double thiation occurred resulting in the isolation of the 2,5-dithione **15** in 75% yield.

As an alternate leaving group in these displacement reactions, we investigated the replacement of the morpholinyl groups in the di-4-morpholinylphosphinyloxy function with phenoxy groups. When the anion of lactam **1** was phosphorylated[7] with diphenyl phosphorochloridate, the desired imidoyl phosphate **17** could not be isolated. The presence of **17** in the reaction mixture is, however, suggested by the fact that quenching the mixture with methylamine resulted in the formation of the amidine **9a** (20% yield).

Experimental Section

7-Chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-one[12] (1) from the Hydrolysis of 7-Chloro-2-(di-4-morpholinyl)-phosphinyloxy-5-phenyl-3*H*-1,4-benzodiazepine (6).[7] A solution of 245 mg (0.5 mmol) of **6** in 5 ml of tetrahydrofuran was stirred with 1.5 ml of water for 7 days. Tetrahydrofuran was evaporated. The residue was partitioned between water and methylene chloride. The organic layer was dried and evaporated. The products were separated by preparative TLC on four silica gel plates developed in 10% methanol–ethyl acetate. The front band (R_f 0.69) was collected, eluted with

10% methanol–ethyl acetate, and evaporated. Crystallization of the residue from ether gave 70 mg (52%) of colorless prisms, mp 215–217 °C. This material was identified as 1 by TLC, mixture melting point, and comparison of infrared spectra with an authentic sample.[12]

The major by-product (R_f 0.53) was collected, eluted with 10% methanol–ethyl acetate, and evaporated. Crystallization of the residue from hexane gave 14 mg (8%) of colorless solids, mp 75–85 °C dec. This material was identified as 7-chloro-2-(4-morpholinyl)-5-phenyl-3*H*-1,4-benzodiazepine (**3**) by TLC, mixture melting point, and comparison of infrared spectra with **3** prepared below.

When this experiment was repeated with heating of the aqueous tetrahydrofuran solution at reflux for 30 h instead of the 7 days at room temperature, we obtained **1** and **3** in 26 and 21%, respectively.

8-Chloro-1-methyl-6-phenyl-4*H*-*s*-triazolo[4,3-*a*][1,4]benzodiazepine (2).[3c] **A. From 6.** To a solution of 74 mg (1.0 mmol) of acethydrazide in 5 ml of butanol was added 245 mg (0.5 mmol) of 7-chloro-2-(di-4-morpholinyl)phosphinyloxy-5-phenyl-3*H*-1,4-benzodiazepine (**6**). The mixture was heated to reflux for 1 h. The solvent was evaporated and the residue was partitioned between methylene chloride and water. The methylene chloride layer was washed with water, dried, and evaporated. The residue was crystallized from methylene chloride–ether to give, in two crops, 124 mg (80%) of **2**, mp 226–228 °C. This material was found identical (TLC, mixture melting point, ir) with a sample prepared by the literature[3c] procedure.

B. From 1 without Isolation of Intermediates. To a solution of 1.08 g (4.0 mmol) of 7-chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-one (**1**) in 20 ml of dry tetrahydrofuran at room temperature was added 230 mg of a 50% dispersion of sodium hydride in oil (4.8 mmol of hydride). The mixture was warmed gently on the steam bath for approximately 1 h until hydrogen evolution stopped. Di-4-morpholinylphosphinic chloride (**16**, 1.53 g, 6.0 mmol) was added and the resulting mixture was stirred at room temperature for 2 h. To this mixture was then added a solution of 593 mg (8 mmol) of acethydrazide in 5 ml of butanol and stirring was continued at room temperature for 10 min. Solvents were evaporated and the residue was dissolved in 10 ml of butanol and heated to reflux for 1 h. Butanol was evaporated and the residue was partitioned between methylene chloride and water. The methylene chloride layer was dried and evaporated. The residue was crystallized from methylene chloride–ether to give 745 mg (62%) of **2**, mp 223–225 °C. This material was identical with the material prepared above by TLC and comparison of infrared spectra.

7-Chloro-2-(4-morpholinyl)-5-phenyl-3*H*-1,4-benzodiazepine (3). A. From 6 with Morpholine. To a stirred solution of 4.9 g (10 mmol) of **6** in 220 ml of tetrahydrofuran at room temperature was added 2.2 g (25 mmol) of morpholine. Stirring was continued at room temperature overnight. Tetrahydrofuran was evaporated. The residue was partitioned between water and methylene chloride. The organic layer was dried and evaporated. Crystallization of the residue from hexane over dry ice gave 2.5 g (74%) of the desired product. Recrystallization from hexane afforded colorless prisms: mp 80–90 °C (indefinite); ir (KBr) 1560 and 1585 cm^{-1}; uv max (2-PrOH) 233 nm (ϵ 27 250), 272 (18 650), 285 (sh, 17 400), and 351 (3100); mass spectrum *m/e* 339 (M^+).

Anal. Calcd for $C_{19}H_{18}ClN_3O$: C, 67.16; H, 5.34; N, 12.37. Found: C, 67.04; H, 5.36; N, 12.10.

B. From 6 in Aqueous Tetrahydrofuran. Compound **3** occurred as a significant by-product in the hydrolysis of **6** described above.

C. From the Pyrolysis of 6. A suspension of 978 mg (2.0 mmol) of **6** in 10 ml of 1,2,4-trichlorobenzene (bp 214 °C) was heated to reflux for 0.5 h. The resulting solution was concentrated at 80–90 °C and applied directly on 24 preparative TLC plates, then developed in methanol–ethyl acetate (1:10 v/v). The main product **3** (R_f 0.59) was isolated and crystallized from petroleum ether to give 233 mg (26%) of colorless prisms, mp 80–90 °C (indefinite). A major by-product **4** (R_f 0.74) was also isolated and crystallized from petroleum ether to give 153 mg (17%) of light yellow prisms, mp 178–180 °C. This material was found to be identical (TLC, mixture melting point) with **4** as prepared below.

3-Amino-6-chloro-2-(4-morpholinyl)-4-phenylquinoline (4). A. From 8. A mixture of 245 mg (0.5 mmol) of 3-amino-6-chloro-2-(di-4-morpholinyl)phosphinyloxy-4-phenylquinoline (**8**)[7] and 5 ml of morpholine was heated to reflux for 46 h. Morpholine was evaporated. The gum was separated by preparative TLC on five silica gel plates developed in ether. The desired product (R_f 0.81) was isolated and crystallized from ethyl acetate to give 20 mg (12%) of light yellow prisms: mp 178–180 °C; ir (KBr) 3330 (broad), 1585, and 1410 cm^{-1}; uv max (2-PrOH) 232 nm (ϵ 32 800), 255 (37 000), and 353 (11 300); mass spectrum *m/e* 339 (M^+).

Anal. Calcd for $C_{19}H_{18}ClN_3O$: C, 67.16; H, 5.34; N, 12.37. Found: C, 67.34; H, 5.28; N, 12.68.

B. From 3. A solution of 170 mg (0.5 mmol) of **3** in 2 ml of 1,2,4-trichlorobenzene containing 0.1 mmol of *p*-toluenesulfonic acid was heated to reflux for 4 h. The mixture was separated by preparative TLC on five silica gel plates developed in ether. The desired product **4** (R_f 0.81) was isolated and crystallized from ethyl acetate to give 60 mg (35%) of light yellow prisms, mp 178–180 °C. Mixture melting point with **4** from A above was undepressed.

7-Chloro-2-methoxy-5-phenyl-3*H*-1,4-benzodiazepine (5a).[8,13] To a solution of 245 mg (0.5 mmol) of **6** in 5 ml of methanol at room temperature was added 82 mg (1.5 mmol) of sodium methoxide. The mixture was left at room temperature overnight. Methanol was evaporated and the residue was slurried with ether. Insoluble salts were removed by filtration. The clear ether solution was evaporated. Crystallization of the residue from petroleum ether yielded 124 mg (87%) of **5a**, mp 94–97 °C. This material was found to be identical (TLC, mixture melting point) with a reference[13] sample of **5a**.

7-Chloro-2-(2-hydroxyethoxy)-5-phenyl-3*H*-1,4-benzodiazepine (5b). A suspension of 1.95 g (4.0 mmol) of **6** in 10 ml of ethylene glycol containing 4 ml of triethylamine was heated on a steam bath for 2 h. A clear solution formed soon after heating began. Triethylamine was removed in vacuo. The ethylene glycol solution was poured into ice water precipitating solids which were collected and washed thoroughly with water. Remaining water was removed from the solid by dissolving the solid in ether, drying over sodium sulfate, and evaporation of ether. Crystallization of the residue from ether–hexane gave 1.03 g (82%) of colorless prisms: mp 142–144 °C; ir (KBr) 3250 and 1645 cm^{-1}; uv max (2-PrOH) 218 nm (ϵ 33 200), 255 (sh, 14 800), and 322 (2260); NMR ($CDCl_3$) δ 2.96 (t, 1, OH), 3.9 (m, 2, CH_2OH), 4.11 (broad s, 2 CH_2), 4.4 (m, 2, CH_2O), and 7.2–7.6 ppm (m, 8, aromatic).

Anal. Calcd for $C_{17}H_{15}ClN_2O_2$: C, 64.87; H, 4.80; N, 8.90. Found: C, 64.83; H, 5.08; N, 9.05.

7-Chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepine-2-thione (7).[3b] To a stirred solution of 245 mg (0.50 mmol) of **6** in 10 ml of tetrahydrofuran containing 0.5 ml of triethylamine at room temperature was introduced a stream of hydrogen sulfide gas until TLC indicated that all the starting material was consumed (15 min). Tetrahydrofuran was evaporated. The residue was partitioned between methylene chloride and water. The methylene chloride layer was dried and evaporated. Crystallization of the residue from methanol yielded in two crops 115 mg (78%) of **7**, mp 243–245 °C. This material was identified by TLC, mixture melting point, and ir comparisons with an authentic sample.

7-Chloro-2-methylamino-5-phenyl-3*H*-1,4-benzodiazepine (9a).[14] **A. From Di-4-morpholinylphosphinyloxy Imine 6.** To a solution of 487 mg (1.0 mmol) of **6** in 10 ml of tetrahydrofuran at room temperature was introduced a stream of methylamine gas for 10 min. Solids precipitated during the addition. The solvent was evaporated and the residue was partitioned between methylene chloride and water. The methylene chloride layer was dried and evaporated. Crystallization of the residue from methylene chloride–hexane yielded, in two crops, 275 mg (96%) of **9a**, mp 245–247 °C. This material was identified by TLC, mixture melting point, and ir comparisons with an authentic sample.[14]

B. By Way of Diphenoxyphosphinyloxy Imine 17. To a solution of 2.7 g (10 mmol) of **1** in 100 ml of dry tetrahydrofuran at room temperature was added 576 mg of 50% dispersion of sodium hydride in mineral oil (12 mmol of hydride). The mixture was warmed gently on the steam bath for approximately 1 h until hydrogen evolution stopped. To this mixture was added 4 g (15 mmol) of diphenyl phosphorochloridate. The mixture was kept at room temperature overnight. Insoluble salts were removed by filtration and the solvent was evaporated. The residue was dissolved in 50 ml of tetrahydrofuran and methylamine gas was bubbled into the solution at room temperature for 0.5 h. Tetrahydrofuran was evaporated and the residue was partitioned between methylene chloride and water. The methylene chloride layer was dried and evaporated. Crystallization from methylene chloride–hexane yielded, in two crops, 540 mg (20%) of **9a**, mp 245–247 °C, identified by TLC, mixture melting point, and comparison of ir spectra.

7-Chloro-2-(2-methoxycarbonyl)hydrazino-5-phenyl-3*H*-1,4-benzodiazepine (9b). To a stirred solution of 9.8 g (20 mmol) of **6** in 200 ml of tetrahydrofuran at room temperature was added 3.6 g (40 mmol) of methyl hydrazinocarboxylate. The resulting orange solution was stirred at room temperature for 2 h. Tetrahydrofuran was evaporated. The residue was partitioned between water and methylene chloride. The methylene chloride layer was dried and evaporated. Crystallization of the residue from ethyl acetate gave 5.8

g (84%) of the product, mp 198–200 °C dec. Recrystallization from ethyl acetate afforded colorless needles: mp 201–203 °C dec; ir (KBr) 3200, 1690, and 1610 cm^{-1}; uv max (2-PrOH) 210 nm (sh, ϵ 18 600), 230 (sh, 15 000), 258 (13 350), and 337 (900).

Anal. Calcd for $C_{17}H_{15}ClN_4O_2$: C, 59.57; H, 4.41; N, 16.35. Found: C, 59.30; H, 4.47; N, 16.32.

7-Chloro-1,3-dihydro-2-nitromethylene-5-phenyl-2*H*-1,4-benzodiazepine (10).[9] To a mixture of 1.0 ml of nitromethane and 5 ml of dry dimethylformamide was added 53 mg of a 50% dispersion of sodium hydride in mineral oil (1.1 mmol hydride). After 1 h at room temperature, under nitrogen, 489 mg (1.0 mmol) of **6** was added. After stirring at room temperature for 2 h, dimethylformamide was evaporated (about 80 °C). The residue was partitioned between methylene chloride and an aqueous layer which is acidified with a slight excess of acetic acid. The methylene chloride layer was dried with anhydrous sodium sulfate and evaporated. Separation of the product mixture by preparative TLC (silica gel, developed in 10% methanol in ethyl acetate v/v) afforded pure **10** (R_f 0.72), which upon crystallization from methanol weighed 85 mg (27%), mp 178–180 °C. This material is identical with a reference sample[9] of **10** (TLC, mixture melting point, ir).

7-Chloro-1,3-dihydro-2-(dimethoxymalonylidene)-5-phenyl-2*H*-1,4-benzodiazepine (11).[5] To a solution of 489 mg (1.0 mmol) of **6** in 5 ml of dry dimethylformamide at room temperature was added 130 mg (1.15 mmol) of potassium *tert*-butyl alcoholate and 0.5 ml of dimethyl malonate. The resulting dark mixture was kept at room temperature for 2 h, then warmed on the steam bath for 0.5 h. The solvent was evaporated and the desired product (R_f 0.62, ether) was isolated by using preparative thin layer chromatography. Crystallization from 2-propanol yielded 50 mg (13%) of **11**, mp 130–133 °C. This material was identical with an authentic sample[5] of **11** by TLC and comparision of infrared spectra.

3-Amino-6-chloro-2-methylthio-4-phenylquinoline (12). To a stirred solution of 489 mg (1.0 mmol) of 3-amino-6-chloro-2-(di-4-morpholinyl)phosphinyloxy-4-phenylquinoline (**8**) in 30 ml of dry tetrahydrofuran was added 4 ml of a 1 M solution of sodium salt of methyl mercaptan in Cellosolve. The reaction mixture was heated to reflux for 2 h. The resulting suspension was then allowed to cool to room temperature at which time the insoluble salts were removed by filtration. The filtrate was concentrated to an oily gum. The gum was separated by preparative TLC (six silica gel plates developed in a 1:9 v/v mixture of ether and benzene). The desired product (R_f 0.80) was isolated and crystallized from ether–hexane. A total of 79 mg (26%) of light yellow prisms was collected: mp 115–117 °C; ir (KBr) 3470 and 3380 (NH_2) and 1610 and 1485 cm^{-1} (aromatic).

Anal. Calcd for $C_{16}H_{13}ClN_2S$: C, 63.89; H, 4.57; N, 9.31. Found: C, 64.02; H, 4.37; N, 9.63.

7-Chloro-2,5-bis(methylamino)-3*H*-1,4-benzodiazepine (14). A solution of 1.00 g (2.2 mmol) of 7-chloro-5-(di-4-morpholinyl) phosphinyloxy-2-methylamino-3*H*-1,4-benzodiazepine (**13**) in 30 ml of a 3.8 M solution of methylamine in tetrahydrofuran was heated in a stoppered glass pressure bottle on a steam bath for 24 h. The solution was concentrated to a gum. The gum was dissolved in a small volume of ethanol. Addition of ethanolic hydrogen chloride followed by ether afforded 500 mg of hydrochloride salt, mp 276–278 °C.

The salt was dissolved in water and basified with aqueous ammonia to liberate the free base. The base was isolated by extraction with methylene chloride. Crystallization from methylene chloride afforded 250 mg (48%) of colorless prisms, mp 235–237 °C. Recrystallization from ethanol raised the mp to 248–250 °C; ir (KBr) 3275 and 3200 cm^{-1} (NH) and broad unresolved bands between 1590 and 1490 cm^{-1}; uv max (CH_3OH) 218 nm (sh, ϵ 18 500), 272 (14 400), and 319 (2900); mass spectrum *m/e* 236 (M^+).

Anal. Calcd for $C_{11}H_{13}ClN_4$: C, 55.82; H, 5.54; N, 23.67. Found: C, 55.53; H, 5.44; N, 23.72.

7-Chloro-1,2,3,4-tetrahydro-5*H*-2,5-dithione (15). To a stirred suspension of 442 mg (1.0 mmol) of 7-chloro-5-(di-4-morpholinyl)-phosphinyloxy-2-methylamino-3*H*-1,4-benzodiazepine (**13**) and 1.0 ml of triethylamine in 50 ml of dry tetrahydrofuran at room temperature was introduced a stream of bubbles of hydrogen sulfide gas for 1 h. Solids gradually dissolved and solution turned yellow. The solution was allowed to stand at room temperature overnight. Tetrahydrofuran was evaporated. The residue was stirred with 50 ml of water and 50 ml of methylene chloride. Solids which precipitated were collected and washed with methylene chloride to give 180 mg (75%) of **15**, mp 273–274 °C dec. Recrystallizations from methanol afforded yellow needles: mp 273 ° dec; ir (KBr) 3150, 1550, 1465, 1380, 1185, and 1165 cm^{-1}; uv max (CH_3OH) 210 nm (ϵ 22 900) 230 (sh, 14 500), 303 (21 100), and 342 (sh, 11 100); mass spectrum *m/e* 242 (M^+); NMR (Me_2SO-d_6) δ 4.18 (broad s, 2, CH_2), 7.23 (d, J = 9 Hz, 1, H-9), 7.61 (dd, 1, H-8), 8.04 (d, J = 2.5 Hz, 1, H-6), 11.22 (broad, 1, NH), and 12.50 ppm (broad, 1, NH).

Anal. Calcd for $C_9H_7ClN_2S_2$: C, 44.53; H, 2.91; N, 11.54; Cl, 14.60; S, 26.42. Found: C, 44.65; H, 3.27; N, 11.52; Cl, 14.50; S, 26.16.

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Registry No.—**3,** 59318-08-0; **4,** 59318-09-1; **5b,** 59318-10-4; **6,** 59318-11-5; **8,** 59318-12-6; **9b,** 59318-13-7; **12,** 59163-16-5; **13,** 59318-14-8; **14,** 59318-15-9; **14** HCl, 59318-16-0; **15,** 59318-17-1; morpholine, 110-91-8; ethylene glycol, 107-21-1; methyl hydrazinocarboxylate, 6294-89-9.

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