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Quinazolines II. (1) Metal Hydride Reductions

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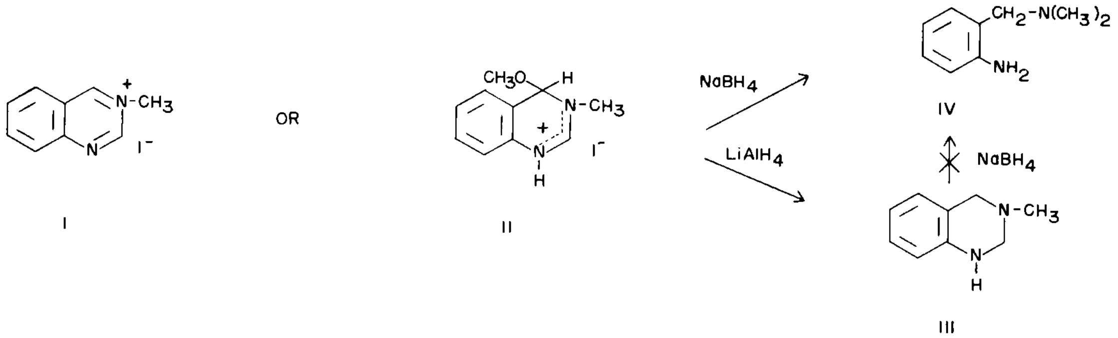
The following sodium borohydride reductions are reported: 3-methylquinazolium iodide (I) or its methanolate (II) ⟶ N^{α},N^{α}-dimethyl-α,2-toluenediamine; quinazoline ⟶ 3,4-dihydroquinazoline or 1,2,3,4-tetrahydroquinazoline (V). The following lithium aluminum hydride reductions are reported: I or II ⟶ 3-methyl-1,2,3,4-tetrahydroquinazoline; quinazoline ⟶ V + N^{α}-methyl-α,2-toluenediamine (VI); 4-chloroquinazoline ⟶ VI; 2-chloroquinazoline ⟶ VI; 2,4-dichloroquinazoline ⟶ V; 2-chloro-4-phenylquinazoline ⟶ 4-phenyl-3,4-dihydroquinazoline; 2-phenyl-4-chloroquinazoline ⟶ 2-phenyl-3,4-dihydroquinazoline or N^{α}-benzyl-α,2-toluenediamine; 4-methoxyquinazoline ⟶ 4-methoxy-1,2-dihydroquinazoline; 4-phenoxyquinazoline ⟶ 4-phenoxy-1,2-dihydroquinazoline; 4-thiophenoxyquinazoline ⟶ VI.

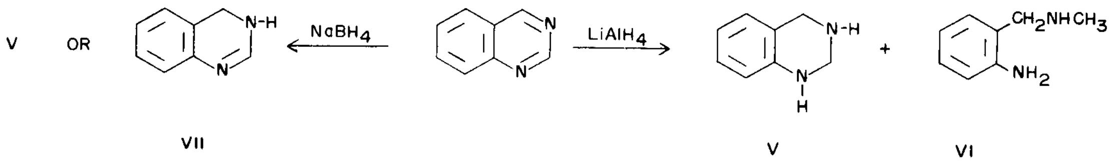
In attempting the synthesis of 3-methyl-1,2,3,4-tetrahydroquinazoline (III) by the sodium borohydride reduction of 3-methylquinazolinium iodide (I) or its methanolate (II) (3), we have obtained low yields of N^{α},N^{α}-dimethyl-α,2-toluenediamine (IV) instead of the anticipated reduced heterocycle. However, reduction of I or II with lithium aluminum hydride gave III and no detectable quantity of the reductive cleavage product IV. Attempted reduction of III with sodium borohydride resulted in its recovery thus indicating that III is an improbable intermediate in the sodium borohydride reduction of the quinazolinium salts (I and II). These earlier observations have prompted us to study the metal hydride reductions (4) of a variety of quinazoline derivatives, and the results of our investigation are reported in this paper.

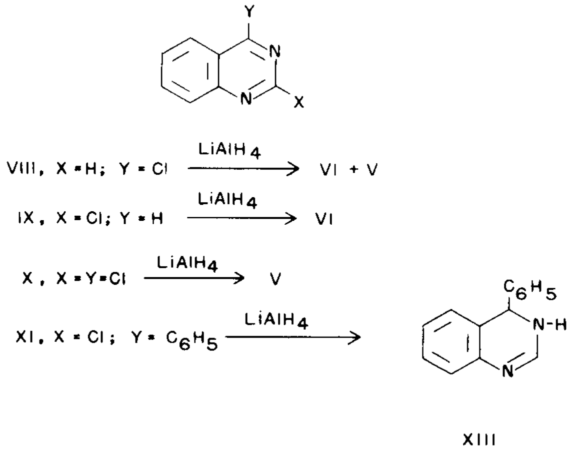
Prolonged reduction of quinazoline with lithium aluminum hydride afforded a mixture consisting of 45% of 1,2,3,4-tetrahydroquinazoline (V) and 23% of N^{α}-methyl-α,2-toluenediamine (VI). Shorter reduction times gave only V. Reduction of quinazoline with aqueous sodium borohydride afforded a low yield of 3,4-dihydroquinazoline (VII) when short reaction times were employed. The use of methanolic sodium borohydride and longer reduction times resulted in moderate yields of 1,2,3,4-tetrahydroquinazoline.

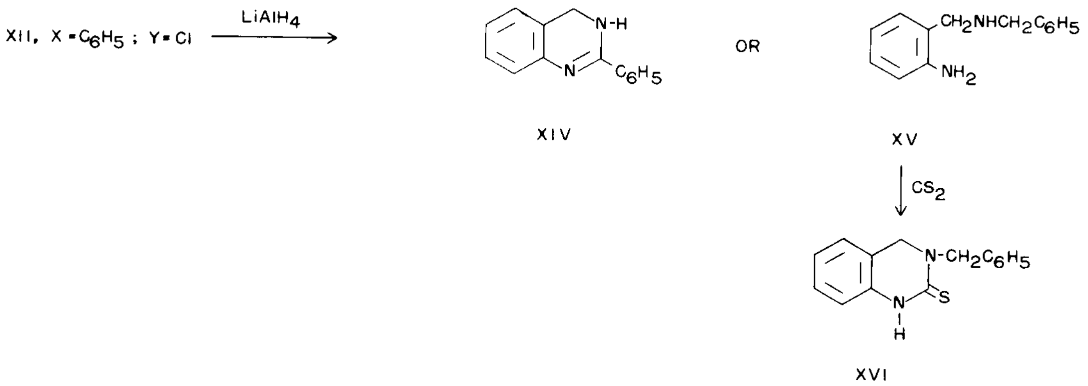
The lithium aluminum hydride reduction of heterochloro substituted quinazolines resulted in hydrogenolysis of the carbon-chlorine bond and further reduction of the hetero-ring. Thus, the diamine (VI) was obtained in good yields from the reduction of 4-chloroquinazoline (VIII) and in poor yields from 2-chloroquinazoline (IX). Tetrahydroquinazoline was also formed in small amounts from the reduction of VIII and was obtained in moderate yields from the reduction of 2,4-dichloroquinazoline (X). The reduction of 2-chloro-4-phenylquinazoline (XI) and 2-phenyl-4-chloroquinazoline (XII) gave good yields of 4-phenyl-3,4-dihydroquinazoline (XIII) and 2-phenyl-3,4-dihydroquinazoline (XIV), respectively. Prolonged reduction of XII with lithium aluminum hydride resulted in the formation of N^{α}-benzyl-α,2-toluenediamine (XV). The structure of XV was established by conversion to 3-benzyl-1,2,3,4-tetrahydroquinazoline-2-thione (XVI) (5). The n.m.r. spectra of XIII and XIV substantiate the previously assigned 3,4-dihydro structures for these compounds (6). The spectrum of compound XIII showed a singlet at τ 4.45 (hydrogen at position 4) 1H; a broad signal at τ 4.24 (NH) 1H and complex absorption at τ 2.36-3.04 (aromatic H plus H at position 2) 10 H. The spectrum of XIV showed a singlet at τ 5.31 (CH_2) 2H, a broad signal at τ 4.34 (NH) 1H and an aromatic multiplet at τ 2.50-3.10 (9H) (7).

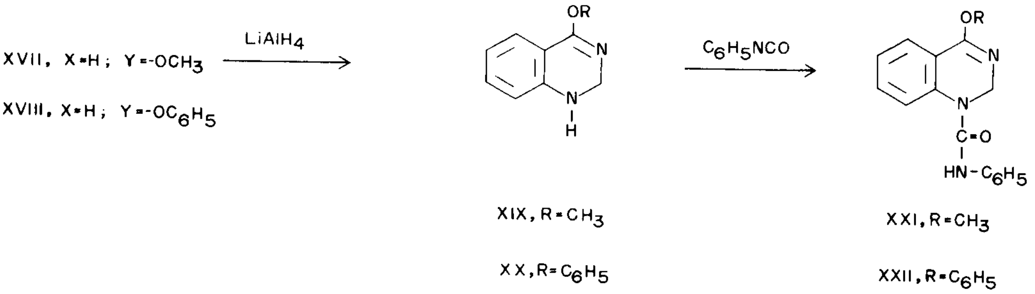
The lithium aluminum hydride reduction of 4-methoxyquinazoline (XVII) and 4-phenoxyquinazoline (XVIII) gave the corresponding 1,2-dihydroquinazoline (XIX and XX). The structural assignments for these dihydrocompounds were made on the basis of their n.m.r. spectra. The reduced methoxy compound could not be purified as the free base but was readily converted to its phenylurea derivative (XXI). The n.m.r. spectrum of XXI was consistent with the assigned structure showing a singlet at τ 6.32 ($-OCH_3$) 3H, a singlet at τ 4.90 ($-CH_2-$) 2H and complex absorption at τ 2.50-3.10 (aromatic H and urea N-H) approximately 10H. 4-Phenoxy-1,2-dihydroquinazoline (XX) was easily purified as the free base and its n.m.r. spectrum showed a broad N-H signal at τ 6.09 (1H), a complex aromatic multiplet at τ 2.28-3.63 (9H) and a doublet centered at τ 5.20 (2H) arising from coupling of the methylene protons to the N-H proton (J = 1.3 c.p.s.). Although the N-H resonance was too broad to show any fine structure, the origin of the doublet was determined by deuterium exchange and by spin decoupling (8). Either exchange of the NH proton by deuterium or irradiation of the NH peak in a double resonance











XXIII, X=H; Y=-SC$_6$H$_5$ $\xrightarrow{\text{LiAlH}_4}$ VI

experiment caused collapse of the CH_2 doublet to a singlet. The n.m.r. spectrum of the phenylurea derivative (XXII) also provided evidence in support of the assigned structure. The CH_2 protons of XXII appeared as a singlet at τ 4.71 (2H), and a multiplet (aromatic protons and urea NH) was observed at τ 2.00-3.00 (15H).

Hydrogenolysis of the sulfur function accompanied by reductive cleavage of the heterocyclic ring was observed in the lithium aluminum hydride reduction of 4-thiophenoxyquinazoline (XXIII), and the diamine (VI) was obtained in 52% yield.

The results of this study do not readily lend themselves to a consistent mechanistic interpretation, and it is felt that speculation in this regard is unwarranted. The extent of reduction with lithium aluminum hydride may be due entirely to the solubility properties of the initially formed complexes.

EXPERIMENTAL (9)

General Procedure for Lithium Aluminum Hydride Reductions.

Unless otherwise noted, the solid quinazolines were added in small portions to magnetically stirred suspensions of powdered lithium aluminum hydride (approximately a 1:2 hydride to quinazoline weight ratio) in anhydrous ether (100 ml. per g. of hydride). The addition was conducted at a rate that maintained gentle reflux, and the reaction mixtures were then heated under reflux for the specified times. Water (twice the weight of hydride) was added dropwise followed by one half the volume of 6*N* sodium hydroxide. Stirring was continued for several hours following hydrolysis. The inorganic salts were filtered off and washed with a large volume of ether. The combined ether solutions were dried over magnesium sulfate.

Reductions of 3-Methylquinazolinium Iodide (I). A. Sodium Borohydride.

The quaternary salt (10) (10 g.) was added in small portions to an ice cooled, stirred solution of 5 g. of sodium borohydride in 50 ml. of water. After stirring at room temperature for one hour, the oily product was extracted with ether. The dried solution was evaporated and the residue distilled to give 1.8 g. (33%) of N^{α},N^{α}-dimethyl-α,2-toluenediamine (IV), b.p. 114-124° (18 mm.), lit. (11) b.p. 107° (14 mm.). No pure products could be isolated from the distillation residue.

The *dipicrate* of IV was recrystallized from ethanol as orange crystals, m.p. 165-167°, and was identical (infrared spectrum and mixed melting point) with that prepared from an authentic sample (11).

Anal. Calcd. for $C_{21}H_{20}N_8O_{14}$: C, 41.45; H, 3.31; N, 18.42. Found: C, 41.85; H, 3.10; N, 18.66.

B. Lithium Aluminum Hydride.

The salt (12.1 g.) was reduced for 3.3 hours. Trituration of the oily product with ligroin gave 2.86 g. (46%) of crude 3-methyl-1,2,3,4-tetrahydroquinazoline (III), m.p. 75-79°, lit. (4b) m.p. 83-84°.

The *picrate* was recrystallized from ethanol, m.p. 133-134°, lit. (4b) m.p. 134°. It gave the correct elemental analysis.

Reductions of 3-Methylquinazolinum Iodide "Methanolate" (II). A. Sodium Borohydride.

The reduction of 3.0 g. of the salt (3) by the same procedure that was employed for the reduction of I resulted in the formation of an oil. The crude product was treated with 2 ml. of phenyl isothiocyanate. After the initial exothermic reaction had subsided, the reaction mixture was warmed briefly on the steam bath. Petroleum ether was added and decanted from the gummy product which was dissolved in hot ethanol. Cooling gave 0.96 g. (34%) of the phenylthiourea derivative of N^{α},N^{α}-dimethyl-α,2-toluenediamine, m.p. 164-167°. Recrystallization from ethanol gave white crystals, m.p. 171-172°. The product was identical with that prepared from the authentic diamine (11).

Anal. Calcd. for $C_{16}H_{19}N_3S$: C, 67.33; H, 6.71; N, 14.72; S, 11.23. Found: C, 67.34; H, 6.54; N, 14.55; S, 11.50.

B. Lithium Aluminum Hydride.

Reduction of 5.0 g. of II for 5 hours gave 4.8 g. (81%) of 3-methyl-1,2,3,4-tetrahydroquinazoline picrate, m.p. 120-123°. One recrystallization from ethanol gave material with a melting point of 129-131° that was identified by its infrared spectrum.

Attempted Reduction of 3-Methyl-1,2,3,4-tetrahydroquinazoline (III) with Sodium Borohydride.

One gram of III was added to a stirred solution of 1 g. of sodium borohydride in 10 ml. of water. After stirring for 4 hours at room temperature, 10 ml. of methanol was added to dissolve the suspended material. An additional 0.5 g. of sodium borohydride was added and stirring was continued for 2 hours. Water (20 ml.) was added and the resultant mixture was extracted with ether. Evaporation of the combined extracts resulted in recovery of starting material, m.p. 70-79°.

Reductions of Quinazoline. A. Lithium Aluminum Hydride.

Quinazoline (2.00 g.) in 25 ml. of ether was added to the lithium aluminum hydride suspension at a rate sufficient to maintain gentle reflux. The reaction mixture was then heated under reflux for 20 hours. The oily product (1.97 g.) was treated with 100 ml. of saturated ethanolic picric acid solution to give 2.49 g. (45%) of crude 1,2,3,4-tetrahydroquinazoline picrate, m.p. 183-184°. Recrystallization from methanol gave yellow crystals, m.p. 195-197°. The picrate was identical (mixed melting point and infrared spectrum) with that prepared from an authentic sample (12) of tetrahydroquinazoline.

Anal. Calcd. for $C_{14}H_{13}N_5O_7$: C, 46.28; H, 3.61; N, 19.28. Found: C, 46.43; H, 3.36; N, 19.10.

Concentration of the filtrate from the picrate preparation gave 2.06 g. (23%) of N^{α}-methyl-α,2-toluenediamine dipicrate, m.p. 152-153°. Recrystallization from ethanol gave the pure picrate, m.p. 155-156°, which was identical (mixed melting point and infrared spectrum) with that prepared from the authentic diamine (4b).

Anal. Calcd. for $C_{20}H_{18}N_8O_{14}$: C, 40.41; H, 3.05; N, 18.85. Found: C, 40.48; H, 3.26; N, 19.18.

When the reduction was conducted for a 2 hour reflux period, the only product that could be isolated was 64% of crude tetrahydroquinazoline picrate, m.p. 182-183°.

B. Aqueous Sodium Borohydride.

One gram of sodium borohydride was added to a stirred solution of 1.0 g. of quinazoline in 10 ml. of water. After stirring for 10 minutes, the reaction mixture was extracted with ether. Evaporation of the dried solution gave a gummy product that was dissolved in hot benzene and treated with ligroin until cloudy. The solution slowly deposited 3,4-dihydroquinazoline, wt. 0.20 g. (18%), m.p. 121-124°, lit. (13) m.p. 127°. The *picrate* had a melting point of 216-218°, lit. (13) m.p. 215°. Evaporation of the benzene-ligroin solution gave a dark oil that resisted crystallization and did not form a crystalline picrate.

C. Methanolic Sodium Borohydride.

Two grams of sodium borohydride was added to a stirred, ice-cooled solution of 2.0 g. of quinazoline in 20 ml. of dry methanol. After stirring for 1 hour at 0° and 1 hour at room temperature, the solution was diluted with water and extracted with ether. Evaporation of the dried ether solution gave a gum that could not be crystallized. Treatment with ethanolic picric acid gave 2.4 g. (51%) of crude tetrahydroquinazoline picrate, m.p. 180-181°. One recrystallization from methanol afforded material with a melting point of 190-191° which was identified by its infrared spectrum.

Lithium Aluminum Hydride Reductions of 4-Chloroquinazoline. A.

The chloro compound (14) (4.00 g.) was reduced for 4 hours. The dried ether solution was treated with anhydrous hydrogen chloride to precipitate a gummy hydrochloride. Trituration with 50 ml. of 1:1 ethanol-ether solution gave 3.6 g. (71%) of N^{α}-methyl-α,2-toluenediamine dihydrochloride, m.p. 230-232°. Several recrystallizations from methanol gave the pure salt, m.p. 236-238°, lit. (4b) m.p. 218°. The infrared spectrum was identical with that of an authentic sample.

Anal. Calcd. for $C_8H_{14}N_2Cl_2$: C, 45.94; H, 6.75; N, 13.40; Cl, 33.91. Found: C, 46.12; H, 6.62; N, 13.17; Cl, 34.00.

B. Reduction of 10.0 g. of the chloro compound under analagous conditions gave 5.1 g. (62%) of N^{α}-methyl-α,2-toluenediamine, b.p. 125-130° (16 mm.) lit. (4b) b.p. 114-118° (10 mm.). The dipicrate had a melting point and mixed melting point of 152-153°.

C. Treatment of the crude product from the reduction of 4.50 g. of the chloro compound with 180 ml. of saturated ethanolic picric acid gave 0.74 g. of crude tetrahydroquinazoline picrate, m.p. 175-178°, which on recrystallization from methanol gave pure material of melting point and mixed melting point, 193-194°. Concentration of the filtrate from the picrate preparation gave 6.96 g. (43%) of crude N$^{\alpha}$-methyl-α,2-toluenediamine dipicrate, m.p. 149-150°, which was identified by its infrared spectrum.

Lithium Aluminum Hydride Reduction of 2-Chloroquinazoline.

The chloro compound (6b) (1.48 g.) was reduced for 2 hours to give a dark oil that afforded 0.96 g. (18%) of crude N$^{\alpha}$-methyl-α,2-toluenediamine dipicrate (identified by its infrared spectrum), m.p. 147-149°.

Lithium Aluminum Hydride Reduction of 2,4-Dichloroquinazoline.

The dichloro compound (14) (5.00 g.) was reduced for 4 hours to give an oil that afforded 4.0 g. (44%) of crude tetrahydroquinazoline picrate (identified by its infrared spectrum), m.p. 183-184°.

Lithium Aluminum Hydride Reduction of 2-Chloro-4-Phenylquinazoline.

The chloro compound (6b) (2.2 g.) was reduced for 3 hours to give 1.2 g. (64%) of crude 4-phenyl-3,4-dihydroquinazoline, m.p. 155-160°. Recrystallization from benzene gave white crystals, m.p. 163-164°, lit. (6b) m.p. 165-166°.

The *picrate* had a melting point of 215-216°, lit. (6b) m.p. 213-214°. The picrate and the free base gave correct elemental analyses.

Lithium Aluminum Hydride Reduction of 2-Phenyl-4-Chloroquinazoline.

A. Reduction of 4.88 g. of the chloro compound (15) for 1.5 hours gave 3.38 g. (80%) of crude 2-phenyl-3,4-dihydroquinazoline, m.p. 131-134°. Recrystallization from ethanol gave white crystals, m.p. 139-141°, lit. (16) m.p. 142-143°.

The *hydrochloride* had a melting point of 255-257°, lit. (16) m.p. 256°.

The *picrate* had a melting point of 180-182°, lit. (6a) m.p. 182-183°. It gave the correct elemental analysis.

B. The chloro compound (3.85 g.) was reduced by heating the reaction mixture under reflux for 6 hours. After standing for an additional 48 hours at room temperature, workup gave crude N$^{\alpha}$-benzyl-α,2-toluenediamine (XV) as a viscous oil which was converted to 3-benzyl-1,2,3,4-tetrahydroquinazoline-2-thione (XVI) by the procedure of Jones and Orth (5). The crude material was obtained in 56% yield, m.p. 200-202°. Recrystallization from ethanol gave white crystals, m.p. 202-203°.

Anal. Calcd. for $C_{15}H_{14}N_2S$: N, 11.02; S, 12.61. Found: N, 10.93; S, 12.67.

An authentic sample (17) of the diamine (XV) was converted to XVI with a melting point and a mixed melting point of 202-204°. The infrared spectra of the two samples were also identical. The n.m.r. spectrum of XVI exhibited two singlet methylene signals at τ 4.45 and τ 4.87 (both integrating for 2H) and an aromatic multiplet at τ 2.34-3.25 (9H).

Apparently, the reported melting point of 112° (5) for XVI is in error.

2-Nitrodibenzylamine.

This compound, which was reduced (17) to the diamine (XV), was conveniently prepared as follows: A mixture consisting of 10.0 g. of *o*-nitrobenzyl chloride, 6.25 g. of benzylamine, 12.9 g. of anhydrous sodium carbonate and 50 ml. of ethanol was stirred and heated under reflux for 12 hours. After the addition of 200 ml. of water, the mixture was extracted with ether. The crude hydrochloride was precipitated from the dried solution with anhydrous hydrogen chloride, wt. 10.3 g., m.p. 211-214°, lit. (17) m.p. 225° (18).

Lithium Aluminum Hydride Reduction of 4-Methoxyquinazoline.

A solution consisting of 2.64 g. of 4-methoxyquinazoline (19) in 35 ml. of dry ether was slowly added to the stirred hydride suspension at a rate to maintain gentle reflux. After heating the reaction mixture under reflux for 1.5 hours, workup afforded 2.01 g. of crude 4-methoxy-1,2-dihydroquinazoline. The oily product resisted crystallization and underwent extensive decomposition during attempted vacuum distillation. It exhibited infrared bands ($CHCl_3$ soln.) at 2.96 μ (NH stretch), 6.05 μ (C=N stretch) and broad absorption at 8.2-8.3 μ (C-O stretch).

The crude material was treated with an equivalent amount of phenyl isocyanate and heated on the steam bath for 10 minutes. The cooled reaction mixture crystallized after trituration with ligroin to give a quantitative yield of the crude *phenylurea derivative* (XXI), m.p. 143-160°. Recrystallization from benzene gave white needles, m.p. 168-169°.

Anal. Calcd. for $C_{16}H_{15}N_3O_2$: C, 68.31; H, 5.37; N, 14.93. Found: C, 68.42; H, 5.67; N, 14.77.

Lithium Aluminum Hydride Reduction of 4-Phenoxyquinazoline.

After reduction for 2 hours, 4.8 g. of the phenoxy compound (20) gave a semi-solid that afforded 3.2 g. (67%) of crude 4-phenoxy-1,2-dihydroquinazoline, m.p. 117-125°, on trituration with cold ethanol. Recrystallization from ethanol gave yellow crystals, m.p. 130-132°.

Anal. Calcd. for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.40; N, 12.50. Found: C, 75.25; H, 5.37; N, 12.53.

The infrared spectrum showed characteristic bands at 2.92 μ (N-H stretch), 6.03 μ (C=N stretch) and broad absorption at 8.1-8.4 μ (C-O stretch).

The phenylurea derivative (XXII) was recrystallized from benzene as white crystals, m.p. 183-184°.

Anal. Calcd. for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.23. Found: C, 73.85; H, 5.28; N, 11.91.

Lithium Aluminum Hydride Reduction of 4-Thiophenoxyquinazoline.

The sulfide (21) (1.75 g.) was reduced for 2 hours. Treatment of the dried ether solution with anhydrous hydrogen chloride gave a hygroscopic product which on recrystallization from ethanol afforded 0.79 g. (52%) of N$^{\alpha}$-methyl-α,2-toluenediamine dihydrochloride, m.p. 222-225° (identified by its infrared spectrum).

Acknowledgment.

This work was supported by a National Science Foundation Undergraduate Research Participation Grant and by a Grant-in-Aid from the Research Foundation of the State University of New York. We also wish to gratefully acknowledge the kindness of the staff of the Sterling-Winthrop Research Institute for the analytical determinations (by Mr. K. Fleischer) and n.m.r. data (by Miss C. Martini). Special thanks are also due Dr. L. D. Colebrook of the University of Rochester for providing the double resonance and deuterium exchange data.

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Received February 8, 1965

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