tube was recrystallized from benzene–light petroleum (bp 60–110°) to give golden yellow plates of **ferrocenyl ferrocenethiolsulfonate,** begins to darken at 180° and melts at 194–195° (dec): ir (KBr) 1320 (s), 1120 cm^{-1} (s); NMR ($CDCl_3$) δ 4.40 (m, 9 H), 4.32 (m, 2 H), 4.21 (s, 5 H), and 4.18 (m, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) 467 (2), 466 ($M\cdot^+$, 7), 402 (52), 306 (22), 304 (24), 272 (24), 233 (21), 218 (36), 217 (100), 186 (29), 153 (39), 121 (40), 56 (31).

Anal. Calcd for $C_{20}H_{18}Fe_2O_2S_2$: C, 51.53; H, 3.89. Found: C, 51.66; H, 3.95.

2,4,6-Trimethylpyridinium Ferrocenesulfonylimino Ylide (22). Ferrocenesulfonyl hydrazide (7.00 g) and 2,4,6-trimethylpyrylium perchlorate[16] (5.68 g) in 95% ethanol (300 ml) were boiled under reflux for 24 hr under nitrogen. The solution was cooled and evaporated in vacuo to ca. 30 ml at 50°. A solution of potassium hydroxide (1.41 g) in water (9 ml) was added dropwise at 0° to the stirred solution. After 30 min at 0° the mixture was filtered cold and the filtrate evaporated onto basic alumina (10 g). The ylide was chromatographed on a column of basic alumina (2 × 45 cm) prepared in benzene. It was eluted with ethyl acetate–ethanol (95:5 v/v) and recrystallized from methanol–ether at −78° to give yellow-orange plates of **2,4,6-trimethylpyridinium ferrocenesulfonylimino ylide** (4.96 g, 52%): mp 180–182° dec; ir (KBr) 1290 (s), 1120 cm^{-1} (s); λ_{max} (EtOH) 212 nm (ε 37 000), 249 (13 360), 350 (730), and 426 nm (206); NMR ($CDCl_3$) δ 7.15 (s, 2 H, H_3 and H_5 of pyr), 4.44 (t, $J_{2,3}$ = 3.3 Hz, 2 H, H_2 and H_5), 4.35 (s, 5 H, H_1'–H_5'), 4.21 (t, $J_{2,3}$ = 3.3 Hz, 2 H, H_3 and H_4), 2.59 (s, 6 H, 2-CH_3 and 6-CH_3), and 2.39 (s, 3 H, 4-CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 385 (7), 384 ($M\cdot^+$, 33), 265 (36), 199 (12), 177 (29), 135 (21), 121 (100).

Anal. Calcd for $C_{18}H_{20}FeN_2O_2S$: C, 56.26; H, 5.24. Found: C, 56.58; H, 5.39.

Decomposition of the Ylide 22. A. Thermolysis. The ylide (0.34 g) in benzene (25 ml, Na dried) was heated at 175° for 10 hr. After cooling, the yellow solution and dark precipitate were removed, the liner was rinsed with benzene (3 × 10 ml), and the product mixture was evaporated onto neutral alumina (3 g). The mixture was chromatographed on a column of neutral alumina (1 × 20 cm). Elution with benzene–ethyl acetate (95:5 and 1:1 v/v) gave 2,4,6-trimethylpyridine (0.068 g, 71%), identical (ir, NMR, and MS) with an authentic sample. Further elution with benzene–ethyl acetate (1:1 v/v) gave ferrocenesulfonamide (0.11 g, 54%), identical (ir and NMR) with an authentic sample. Elution with ethyl acetate–ethanol (95:5 v/v) gave unchanged 2,4,6-trimethylpyridiniumferrocenesulfonylimino ylide (0.038 g, 11%).

B. Photolysis. The ylide (1.00 g) was dissolved in benzene (100 ml, Na dried) in a quartz photolysis vessel equipped with a nitrogen bubbler and drying tube ($MgSO_4$). The solution was purged with nitrogen (dry, O_2 free) for 30 min and then irradiated with 2537-Å lamps in a Rayonet reactor at a temperature of about 40°. Nitrogen was bubbled slowly through the solution during the irradiation. The progress of the photolysis was followed by removing an aliquot at regular intervals, evaporating to dryness under a cone of nitrogen, and observing the ir. After 72 hr no detectable change had occurred in the infrared spectrum. The solution was then removed, the vessel rinsed with benzene (2 × 20 ml), and the combined solutions chromatographed on a column of neutral alumina. Elution with ethyl acetate–ethanol (95:5 v/v) gave only starting ylide (0.72 g, 72%).

Experiments using 3000- and 3500-Å lamps gave similar results.

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Registry No.—6, 57362-98-8; **7,** 41686-87-7; **8,** 57363-01-6; **9,** 57363-02-7; **12,** 57363-08-3; **13,** 57363-07-2; **14,** 57363-00-5; **15,** 57363-03-8; **17,** 57363-06-1; **18,** 57363-05-0; **19,** 57363-04-9; **20,** 57362-99-9; **22,** 57395-85-4; **23,** 57395-86-5; **24,** 57395-90-1; phosphorus oxychloride, 10025-87-3; diammonium ferrocene-1,1′-disulfonate, 12184-14-4; sodium azide, 26628-22-8; cyclohexylamine, 108-91-8; cyclohexane, 110-82-7; mesitylene, 108-67-8; 2,4,6-trimethylpyrylium perchlorate, 940-93-2.

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Interaction of Alkali Metals with Unsaturated Heterocyclic Compounds. II. 2,4-Diphenylquinazoline

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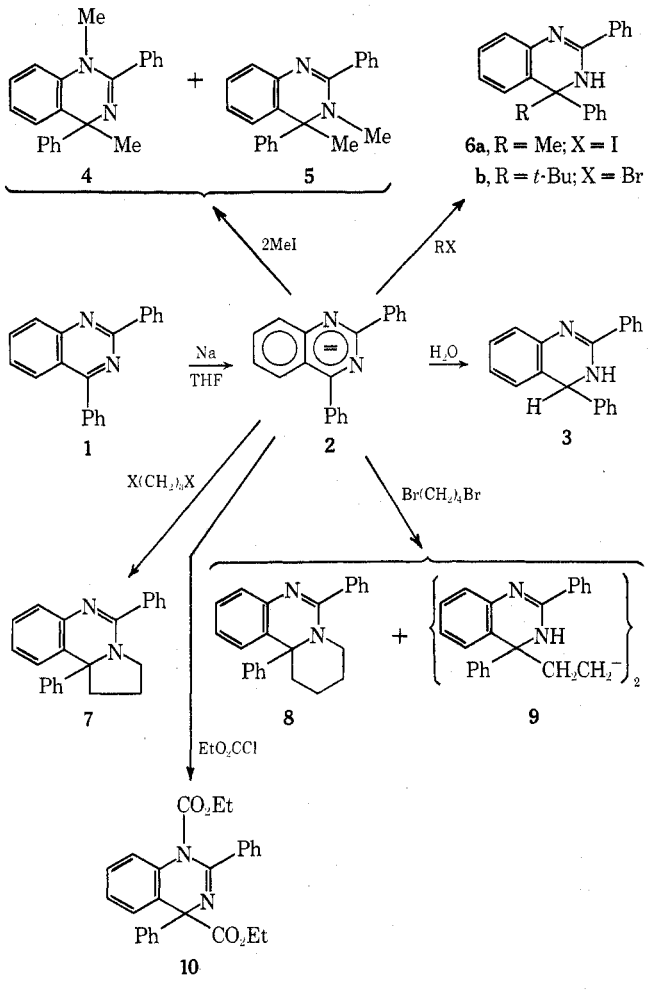
2,4-Diphenylquinazoline (1) is reduced by sodium in tetrahydrofuran to a dianion **2.** Alkylation of this dianion with methyl iodide, *tert*-butyl bromide, 1,3-dihalopropanes, and 1,4-dibromobutane is described as well as acylation with ethyl chloroformate. Generally the alkylation products are 3,4-dihydroquinazoline derivatives but 1,4-dihydro derivatives are isolated in the case of methyl iodide and dimeric products formed by intermolecular alkylation are observed with 1,4-dibromobutane. The products formed by alkylation with *tert*-butyl bromide also contain compounds containing the alkyl group in the benzo ring. These products were also formed by the reaction of 1 with *tert*-butyllithium. In the case of acylation only 1,4-dihydroquinazoline derivatives were detected.

The reduction of conjugated bisimines by alkali metals in aprotic solvents has been examined in earlier studies.[1,2] In this report the combination of two imine groups conjugated through a carbon–nitrogen bond is studied by the reductive metalation of 2,4-diphenylquinazoline (1). This compound was selected since it both contained the desired conjugative arrangement and is similar to a compound examined in an earlier report,[2b] 2,3-diphenylquinoxaline.

Only the reduction of 1 in tetrahydrofuran (THF) by sodium was examined in detail, since under these conditions

Scheme I
Reactions of the Dianion from 2,4-Diphenylquinazoline



the dianion **2** (Scheme I) was produced smoothly. In diethyl ether the reduction was very slow and with lithium in THF excessive reduction was obtained.

Protonation of the dianion, **2**, produced 3,4-dihydro-2,4-diphenylquinazoline (**3**). The 3,4-dihydro structure was assigned since the same product was obtained from the lithium aluminum hydride reduction[3] of 2,4-diphenylquinazoline and from the addition of phenylmagnesium bromide to 2-phenylquinazoline.[4]

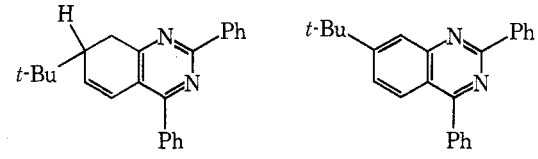
Alkylation of the dianion, **2**, with methyl iodide produced an isomeric mixture of 1,4-dimethyl-1,4-dihydro- and 3,4-dimethyl-3,4-dihydroquinazolines (**4** and **5**), respectively, in the ratio of 2.2:1. Separation was effected by chromatography on alumina and the compounds proved identical with those prepared earlier[5] by a different route and characterized by spectroscopic correlations.

The stepwise nature of the alkylation was indicated by the formation of the monoalkylation product 4-methyl-3,4-dihydro-2,4-diphenylquinazoline (**6a**) when only 1 equiv of the alkylating agent was employed.

An extension of the fused ring system was effected by alkylating **2** with dihaloalkanes. Attachment of a five-membered ring to the 3,4 position (i.e., **7**) was successful with 1,3-dichloro- and 1,3-dibromopropane; the reaction was less efficient with iodide as the leaving group since appreciable amounts of **1** were regenerated. Attempts to fuse a six-membered ring to the quinazoline framework to give **8** by using 1,4-dibromobutane were less satisfactory. While **8** was obtained, competitive intermolecular alkylation occurred giving dimeric product **9** and apparently oligomeric material.

Alkylation of dianion **2** with *tert*-butyl bromide proceeded smoothly to give a reaction mixture containing approximately 75% alkylation product, the remainder being 2,4-diphenylquinazoline (**1**). The main product was 4-*tert*-butyl-2,4-diphenyl-3,4-dihydroquinazoline (**6b**), and an authentic sample was synthesized by treating **1** with *tert*-butyllithium. Like the known 4-*tert*-butyl-3,4-dihydroquinazoline,[4] **6b** was oxidatively dealkylated by alkaline potassium ferricyanide to 2,4-diphenylquinazoline.

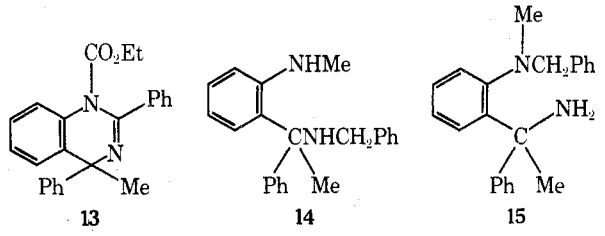
Two additional products, **11** and **12**, were isolated in lower yields from both the alkylation reaction and from the reaction of **1** with *tert*-butyllithium.



Structure **11** was deduced from spectral data. The presence of a pyrimidine ring was indicated by the characteristic[6] downfield chemical shift of the ortho protons of the 2-phenyl substituent and by the presence of a strong absorption band at 1550 cm^{-1} in the infrared spectrum characteristic[7] of the pyrimidine ring. A much more complex pattern exists[5] in the 1500–1650-cm^{-1} region in the case of quinazolines or their 1,4- and 3,4-dihydro derivatives. Integration of the NMR spectrum of **11** showed that the benzo ring of **1** had been alkylated, since, aside from the *tert*-butyl protons, two vinyl, three aliphatic, and ten aromatic protons were present. Substitution in the 4-phenyl (or 2-phenyl) rings would produce quite different ratios. Decoupling of the signals showed that the methylene group was coupled only to the tertiary proton while the latter was coupled to both vinyl protons. This plus the substantial difference in chemical shift of the two vinyl protons ruled out a 5,8-dihydroquinazoline derivative and narrowed the choice to a 5,6- or 7,8-dihydro compound. The 7,8-dihydro structure was selected because of the pronounced downfield position of the methylene resonance and because this chemical shift remained essentially unchanged when the solvent was changed from carbon tetrachloride to benzene-d_6. By analogy with alkyl-substituted pyridine derivatives,[8] these observations indicated that the methylene group was attached to the heterocyclic ring at a carbon α to the nitrogen. If it were attached β to the heteroatom, a marked change in the chemical shift would accompany the change of solvent.

Dehydrogenation of **11** produced 7-*tert*-butyl-2,4-diphenylquinazoline (**12**), thus relating the position of the alkyl group in the two minor products.

Acylation of **2** with ethyl chloroformate produced the single product 1,4-di(ethoxycarbonyl)-2,4-diphenyl-1,4-dihydroquinazoline (**10**). This structure was assigned on the basis of the similarity of its spectroscopic properties[5] to those of **13**. Confirmation of the 1,4-dihydro structure of **13** was obtained by the lithium aluminum hydride reduction[9] of both **13** and **4** to the same product **14**. In the case of the



reduction of **13**, the yield of **14** was 30%; the major product **6a** arose by loss of *N*-ethoxycarbonyl group during reduction. Presumably this involved elimination of formaldehyde from the intermediate *N*-hydroxymethyl derivative.

Structure **14** is compatable with the reported[3] direction of cleavage of the quinazoline ring during metal hydride reduction and with the NMR spectra of model compounds. Thus the N–Me resonance of **14** was observed at δ 2.68 in closer agreement with that of *N*-methylaniline (δ 2.80) than that of *N*-benzyl-*N*-methylaniline (δ 3.00, cf. **15**). The methylene protons of the *N*-benzyl group were observed as an AB quartet centered at δ 3.53 which closely agreed with the chemical shift of the methylene protons of dibenzylamine (δ 3.67) and benzylmethylamine (δ 3.77) but differed markedly from the shift of the corresponding protons of *N*-benzyl-*N*-methylaniline (δ 4.50, cf. **15**). The nonequivalency of the benzylic methylene protons also suggests a proximity of the group to the chiral center as in **14**. Furthermore the mass spectrum of **14** showed the base peak at *m/e* 194 corresponding to $[PhC{\equiv}NCH_2Ph]^+$, essentially the main side chain of **14**.

The mass spectra of the various dihydroquinazolines prepared here showed a simple pattern. Unlike the parent 2,4-diphenylquinazoline (**1**) (or its derivative **12**), the parent ion was relatively small. The major fragmentation resulted from loss of one or the other of the two substituents at the 4 position to give the base peak and a second major fragment. Loss of the 4-phenyl substituent dominated when the second substituent was hydrogen (i.e., **3**) or when the other substituent was part of a ring (i.e., **7** and **8**). When the second substituent was an alkyl group, the $M^+ - R$ fragment formed the base peak and $M^+ - Ph$ a peak of no more than half its intensity.

The presence of ethoxycarbonyl groups introduced additional major fragmentation pathways and differences were observed between a 1- and a 4-ethoxycarbonyl group. The 4-ethoxycarbonyl group was lost in a single step while the 1-ethoxycarbonyl group fragmented stepwise with loss of CO_2 and C_2H_4.

Discussion

The efficient alkylation of dianion **2** with *tert*-butyl bromide is unexpected and indicates that the reaction cannot be regarded simply as a nucleophilic substitution. The similarity between this reaction and that of *tert*-butyllithium with 2,4-diphenylquinazoline suggests that the alkylation proceeds through a halogen–metal exchange with **2** acting as a source of "dissolved" sodium. Thus,

$$2 + t\text{-BuBr} \rightarrow 1 + t\text{-BuNa} + \text{NaBr}$$

$$1 + t\text{-BuNa} \rightarrow \mathbf{6b} + 11 + 12$$

Such exchange reactions with lithium dihydronaphthylide have been described[10] by Screttas. The main product is **6b** formed by nucleophilic addition to the reactive 3,4 bond of **1** and the minor products arise by a "1,6 addition" facilitated by the steric bulk of the attacking nucleophile followed either by protonation to give **11** or by loss of metal hydride to give **12**.

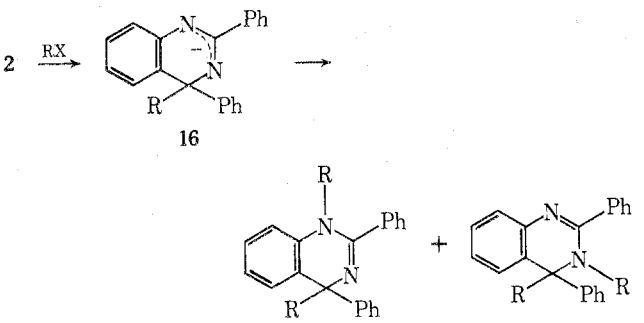
However, an alternative view is that the reaction of **1** with *tert*-butyllithium and **2** with *tert*-butyl bromide are similar since both proceed by one-electron transfer to form a *tert*-butyl radical–diphenylquinazoline radical anion ($Q\cdot^-$) pair. Products then arise by coupling of the radical–radical anion pair with delocalization of the spin density in the radical anion leading to significant amounts of alkylation in the benzo ring. Both reactions are organic redox reactions with the reducing agent being the alkyllithium compound in one case and the dianion **2** in the other.

$$t\text{-BuLi} + 1 \longrightarrow \underbrace{t\text{-Bu}\cdot + Q^-}_{\downarrow\ \text{products}} \longleftarrow 2 + t\text{-BuBr}$$

Insofar as the organolithium compound is concerned, radical intermediates have been detected in the reaction of these organometallic compounds with alkyl halides[11] and with polycyclic aromatic substrates[12]. One-electron transfer mechanisms have been considered for many reactions[13] including that between diaryl ketones and *tert*-butylmagnesium halides[14] and metalation of aromatic compounds by organolithium reagents.[12b]

In the case of the reaction between radical anions and alkyl halides, one-electron reduction is well established[15] as is the facile transfer of electrons from dianions such as **2** to a receptive substrate.[15c]

In any case, the stepwise nature of the alkylation of **2** is evident and similar to that noted earlier.[2b] The marked difference in reactivity between the original dianion **2** and its monoalkylated product is no doubt due to the effective delocalization of the residual charge over the amidine portion of the molecule (i.e., **16**) which leads also to the two dialkylation products observed in those cases where rapid dehydrohalogenation of the alkylating agent does not occur.



16

In the case of 1,3-dihalopropanes and 1,4-dihalobutanes, the monomeric products are necessarily 3,4-dihydro derivatives. The much higher yield of **7** compared to **8** can be the result of several factors. One of these, as has been suggested in a related case,[16] may be unfavorable nonbonded interactions of the substituents attached to the forming six-membered ring which slows its rate of formation sufficiently that competitive intermolecular alkylation occurs leading to **9**.

Experimental Section

Melting points were determined with a Mel-Temp apparatus and are uncorrected. Analyses are by M-H-W Laboratories, Garden City, Mich. Spectra were recorded on Beckman IR-10 (ir), Unicam SP-800 (uv), and Varian T-60 (NMR) instruments. The NMR spectra were determined in $CDCl_3$ and are reported in parts per million downfield from Me_4Si as the internal standard (δ scale). Mass spectra were obtained on an AEI-MS-30 double beam, double focusing mass spectrometer at 70 eV. Samples were inserted via the direct probe and perfluorokerosene was used in the reference beam. In column chromatography, silica gel (70–325 mesh) or neutral aluminum oxide from E. Merck AG was used. Preparative thin layer chromatography was performed with PF-254 aluminium oxide also from E. Merck.

2,4-Diphenylquinazoline (**1**) was prepared by a published procedure.[17] It was purified by distillation [bp 227° (2 mm)] followed be recrystallization from ethanol, white needles, mp 121–122°.

The procedure used to reduce **1** with alkali metals has been described.[18] Titration of aliquot samples showed that the reaction between **1** and sodium in tetrahydrofuran (THF) was complete in 8 hr forming a deep blue solution of the dianion **2**. Generally, complete reaction was ensured by a 12–16-hr reaction time. When diethyl ether (DEE) was used as a reaction solvent, the reduction was inordinately slow. With lithium and THF, the reduction ap-

peared to exceed the requirement of 2 g-atom of Li per mole of **1**. Consequently, only the sodium–THF system was employed in subsequent reactions.

Preparation of 3,4-Dihydro-2,4-diphenylquinazoline (3). The dianion **2** (4.3 mmol) in 100 ml of THF was treated at −78° with 3 ml of water. Decolorization was rapid and after 15 min the reaction product (1.2 g) was isolated by diluting the mixture with water and extracting with ether. Chromatography on silica gel with benzene as eluent gave 0.11 g (9%) of **1** and 1.08 g (88%) of **3**, mp 149–152°. Recrystallization from benzene–petroleum ether gave 0.83 g (70%) of **3**, mp 153–155°, identical with a sample previously prepared[5] by the reaction between phenylmagnesium bromide and 2-phenylquinazoline: mass spectrum *m/e* (rel intensity) 284 (M^+, 19), 283 (11), 208 (18), 207 (100), 180 (15), 129 (19), 77 (38).

In an alternative reduction procedure, a mixture of 0.42 g (1.5 mmol) of **1**, 0.3 g (7.9 mmol) of lithium aluminum hydride, and 125 ml of ether was stirred for 3 days at 20°. Water was added to destroy excess hydride, the mixture was filtered and evaporated, and the residue was recrystallized from pentane giving 0.34 g (80%) of **3**, mp 150–153°.

Alkylation of the Dianion 2 with Methyl Iodide. Preparation of 4, 5, and 6a. A solution of the dianion **2** (0.015 mol) in 250 ml of THF was treated at −78° with 5.2 g (0.037 mol) of methyl iodide. After 1 hr at −78°, the solution was allowed to warm to 20° and stand for 12 hr. Dilution with water and extraction with ether provided the crude product, which was chromatographed on 120 g of silica gel using 2:3 diethyl ether–30–60° petroleum ether. In order of elution, there were obtained 0.6 g (14% recovery) of starting material **1**, 2.83 (60% yield) of crude 1,4-dimethyl-1,4-dihydro-2,4-diphenylquinazoline (**4**), and 1.28 g (27% yield) of crude 3,4-dimethyl-3,4-dihydro-2,4-diphenylquinazoline (**5**).

The crude **4** was recrystallized from cyclohexane–pentane to give 2.28 g (49%), mp 94–95°. A mixture melting point with an authentic sample[5] was undepressed and spectral properties were identical: mass spectrum *m/e* (rel intensity) 312 (M^+, 2), 298 (24), 297 (100), 236 (12), 235 (50), 194 (10), 42 (11).

The crude **5** was purified by several recrystallizations from cyclohexane–pentane, mp 114–115°, undepressed on admixture with an authentic sample,[5] and having identical spectral properties: mass spectrum *m/e* (rel intensity) 312 (M^+, 8), 298 (24), 297 (100), 236 (10), 235 (48), 118 (15), 42 (13).

The dianion **2** (0.005 mol) when treated under the same reaction conditions with 0.70 g (0.005 mol) of methyl iodide changed color from dark blue to red. After 20 min, 8 ml of ethanol was added and the solution became colorless. Addition of water, ether extraction, and evaporation of the extract gave the crude product (1.5 g). Recrystallization from benzene–petroleum ether gave 1.1 g (74%) of 4-methyl-2,4-diphenyl-3,4-dihydroquinazoline (**6a**), as a pale yellow solid, mp 168–170.5°, undepressed on admixture with an authentic[5] sample and having identical spectral properties: mass spectrum *m/e* (rel intensity) 298 (M^+, 5), 284 (22), 283 (100), 222 (9), 221 (53), 77 (12).

With 1,3-Dihalopropane. Preparation of 7. The dianion (3.65 mmol) in 100 ml of THF was cooled to −78° and treated with 0.42 g (3.72 mmol) of 1,3-dichloropropane. The solution slowly became dark green and, after 1 hr, the solution was allowed to warm to 20°. Water was added and the crude product (1.20 g) isolated by extraction with chloroform. Recrystallization from 50 ml of ether–30–60° petroleum ether gave 0.47 g of **7**, mp 136–138°. The mother liquors were concentrated and chromatographed on 30 g of alumina (activity grade III) using petroleum ether containing 20% ether to give an additional 0.52 g of **7**, mp 135–137° (combined yield 84%).

An analytical sample was obtained by recrystallization from diethyl ether, mp 137.5–138°. Spectral properties have been reported[5] except for the mass spectrum: *m/e* (rel intensity) 324 (M^+, 4), 248 (20), 247 (100).

Anal. Calcd for $C_{23}H_{20}N_2$: C, 85.15; H, 6.21; N, 8.63. Found: C, 85.08; H, 6.23; N, 8.39.

Using 1,3-dibromopropane in the above experiment gave an 83% yield of **7** and a 3% recovery of **1** while alkylating the dianion **2** at 20° with 1,3-diodopropane gave a 60% yield of **7** with 40% of **1** being regenerated.

With 1,4-Dibromobutane. Preparation of 8 and 9. The preceding reaction was repeated with 5.1 mmol of **2** in 100 ml of THF and 1.14 g (5.2 mmol) of 1,4-dibromobutane. The crude reaction product, 1.85 g, was chromatographed on 100 g of alumina (activity III) using petroleum ether containing 25% DEE to give in order of elution 0.09 g (6%) of **1**, 0.665 g (39%) of **8**, mp 176–177°, 0.485 g of oligomeric material as a gum, and 0.357 g of an oil identified as **9**.

Recrystallization of **8** from methanol or from petroleum ether–ether gave an allotropic modification with mp 162–163°; mixture melting point with the higher melting form was 176–177°; ir (CCl_4) showed the 3,4-dihydroquinazoline pattern[5] at 1560 (s), 1590 (w), 1615 (w) as well as bands at 1490, 1460, 1400 (C–N), 700 cm^{-1}; NMR δ 1.3–3.7 (methylene envelope, 8), 6.7–7.9 (m, 14, aromatic H); uv (EtOH) λ_{max} (log ϵ) 235 nm (4.31), 305–320 (3.84); mass spectrum *m/e* (rel intensity) 338 (M^+, 7), 282 (13), 262 (18), 261 (100).

Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.27. Found: C, 84.96; H, 6.63; N, 8.07.

The crude **9** was "recrystallized" from benzene to give 0.20 g of an amorphous solid which melted to a viscous gum at 110–113°: ir ($CHCl_3$) 3440 (NH), 2930 (CH), 3,4-dihydroquinazoline pattern[5] at 1560 (s), 1590 (w), 1615 (w) as well as 1490, 690 cm^{-1}; NMR δ 1.3–1.7 (broad s, 4) and 2.0–2.5 (broad s, 4) (methylene H), 6.9–8.1 (m, 28, aromatic H); uv (EtOH) λ_{max} (log ϵ) 234 nm (4.64), 310–320 (4.05); mass spectrum *m/e* (rel intensity) 622 (M^+, 0.3), 341 (12), 340 (38), 284 (41), 283 (100), 282 (9), 281 (11), 221 (8), 77 (41).

Anal. Calcd for $C_{44}H_{38}N_4$: C, 84.85; H, 6.15; N, 9.00. Found: C, 84.61; H, 6.18; N, 8.89.

The crude oligomer was recrystallized from cyclohexane: mp 287–289° dec; ir ($CHCl_3$) 2940, 1,4-dihydroquinazoline pattern 1620 (s), 1600 (w), 1580 (w), and 1480, 1460, 1380, 700 cm^{-1}; NMR δ 1.1–2.4 (methylene envelope, 6), 3.4–3.9 (broad s, 2, CH_2N), 6.3–7.7 (m, 14, aromatic H); the sample was too nonvolatile for a mass spectrum.

With *tert*-Butyl Bromide. Preparation of 6b, 11, and 12. The dianion **2** (0.005 mol) in 125 ml of THF was treated at room temperature with 1.5 g (0.011 mol) of *tert*-butyl bromide. An immediate color change to a dark reddish brown occurred. After 12 hr, water was added and the reaction products (1.88 g) isolated by extraction with ether. Chromatography on 225 g of neutral alumina (activity grade II) using petroleum ether graded to 1:1 petroleum ether–diethyl ether gave, in order of elution, 0.19 g (11%) of **11**, 0.11 g of a mixture (see below), 0.21 g (15%) of regenerated **1**, and 1.02 g (61%) of 4-*tert*-butyl-3,4-dihydro-2,4-diphenylquinazoline (**6b**). Two recrystallizations of the crude **6b** gave 0.61 g of an analytical sample: mp 136–137°; NMR δ 1.30 [s, 9, $C(CH_3)_3$], 5.77 (s, 1, NH), 6.9–8.1 (m, 14, aromatic H); ir ($CHCl_3$) 3440 (NH), 1620, 1590, 1560, 1510, 1490, 1460, 1400, 1370, 930, 840, 690 cm^{-1}; uv (EtOH) λ (log ϵ) 236 (4.30), 265 (3.85), 320 (3.75); mass spectrum *m/e* (rel intensity) 340 (M^+, 0.1), 284 (22), 283 (100), 282 (12), 281 (15), 97 (16), 57 (17).

Anal. Calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.10; N, 8.23. Found: C, 84.49; H, 6.94; N, 8.08.

Treatment of **6b** with hot alkaline potassium ferricyanide[21] led to the loss of the *tert*-butyl group with formation of 2,4-diphenylquinazoline (**1**) in 71% yield.

The crude **11** was purified by recrystallization from methanol to give 0.08 g of an analytical sample: mp 114–115°; NMR[19] δ 1.00 [s, 9, $C(CH_3)_3$], 2.52 [m, 1, CH (H_7), $J_{7,8}$ = 10, $J_{7,8'}$ = 9.5, $J_{6,7}$ = 3.7, $J_{5,7}$ = 2.2 Hz), 3.08 and 3.23 [AB portion of ABX, 2, CH_2 (H_8 and $H_{8'}$), $J_{8,8'}$ = 16.5 Hz], 6.09 [double d, 1, vinyl H (H_6), $J_{5,6}$ = 10 Hz], 6.69 [double d, 1, vinyl H (H_5)], 7.3–7.9 (m, 8, aromatic H), 8.4–8.7 (m, 2, ortho H of 2-Ph) [Spectra were also recorded with solutions of **11** in CCl_4 and C_6D_6 to determine the solvent shift. The chemical shifts of the nonaromatic protons are reported in CCl_4 (C_6D_6): $C(CH_3)_3$ 0.97 (0.78); CH (H_7) 2.33 (2.10); CH_2 (H_8, $H_{8'}$) 2.93, 3.07 (2.90, 3.05); vinyl H_6 6.03 (5.80); vinyl H_5 6.72 (6.65).]; ir ($CHCl_3$) 2970, 1545, 1540, 1420, 1370, 690 cm^{-1}; uv (EtOH) λ (log ϵ) 239 (4.23), 253 (4.30), 301 (4.39); mass spectrum *m/e* (rel intensity) 340 (M^+, 4), 284 (26), 283 (41), 181 (14), 180 (100), 77 (37), 57 (13).

Anal. Calcd for $C_{24}H_{24}N_2$: C, 84.67; H, 7.10; N, 8.23. Found: C, 84.66; H, 7.17; N, 8.25.

The mixture (0.11 g) obtained as the second fraction was chromatographed on a silica gel preparative thin layer plate using 1:1 benzene–petroleum ether. The center cut of the largest band was isolated and rechromatographed on a second plate. The purified material was triturated with pentane to give 30 mg of **12**: mp 100–101.5°; NMR δ 1.43 [s, 9, $C(CH_3)_3$], 7.4–8.2 (m, 11, aromatic H), 8.67–8.87 (m, 2, ortho H of 2-Ph); ir ($CHCl_3$) 2960, 1620, 1560, 1535, 1490, 1400, 1345, 690 cm^{-1}; uv (EtOH) λ (log ϵ) 267 (4.75), 306 (sh, 3.88), 329 (3.79); mass spectrum *m/e* (rel intensity) 339 (13), 338 (M^+, 67), 337 (19), 323 (18), 282 (20), 281 (100), 220 (15), 58 (10).

Anal. Calcd for $C_{24}H_{22}N_2$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.00; H, 6.60; N, 8.25.

Dehydrogenation of 11 to 12. A mixture of 80 mg of **11**, 4 ml of dry decalin, and 200 mg of 5% palladium on carbon was refluxed

for 40 hr.[20] The cooled mixture was diluted with chloroform, filtered free of the catalyst, and steam distilled to remove the solvents. Extraction of the aqueous residue with chloroform provided the crude product which was purified by preparative TLC on silica gel with trichloroethylene as the developing solvent. The third band from the origin was isolated and gave 45 mg (57% yield) of **12**, identical in its spectral properties with the previously isolated material. Recrystallization from pentane gave 23 mg of **12**, mp 104–106°, mmp 102–104°.

Attempts to oxidize **11** with alkaline ferricyanide[21] were unsuccessful.

Acylation of 2 with Ethyl Chloroformate. Preparation of 10. A solution of the dianion (0.005 mol) in 100 ml of THF at −78° was treated with 1.25 g (0.011 mol) of ethyl chloroformate. An immediate color change from blue to purple was observed. The solution was allowed to warm to 20° during which time the color faded to yellow. Addition of water, ether extraction, and evaporation of the extracts gave 1.83 g (85%) of crude **10**, mp 139–141°. Two recrystallisations from ethanol gave an analytical sample, mp 141–142°. Spectral properties have been reported[5] except for the mass spectrum: *m/e* (rel intensity) 356 (25), 355 (100), 312 (19), 311 (75), 284 (17), 283 (75), 281 (19), 205 (10), 180 (10), 77 (9).

Anal. Calcd for $C_{26}H_{24}N_2O_4$: C, 72.88; H, 5.64; N, 6.54. Found: C, 72.91; H, 5.56; N, 6.42.

Reaction of 2,4-Diphenylquinazoline with *tert*-Butyllithium. A solution of 1.0 g (3.4 mmol) of **1** in 200 ml of anhydrous diethyl ether was cooled under nitrogen in a dry ice–2-propanol bath and treated with 6 ml (6 mmol) of a solution of *tert*-butyllithium in *n*-pentane. An immediate dark red-brown color developed. After 1 hr the solution was warmed to 20°, water was added, and the product (1.25 g) was isolated by ether extraction.

The reaction product was chromatographed on silica gel using 2:1 petroleum ether–benzene as eluent and the following products, in order of elution, were isolated and identified by their NMR and ir spectra: 0.27 g (24%) of **11**, mp 113–116°, 57 mg of a 1:1 mixture of **11** and **12**, followed by 25 mg of a mixture of **12** and some unidentified material. Further elution of the column with methylene chloride gave 0.65 g (55%) of **6b** as an oil. Recrystallization from hexane gave 0.39 g of **6b**, mp 134–136°.

The fractions containing **12** were rechromatographed on silica gel (preparative TLC) using trichloroethylene as eluent to give 29 mg of **12**.

The above reaction was repeated using 100 ml of THF as the solvent for **1**. Reaction products were separated by chromatography on silica gel with benzene as eluent. All products except **6b** elute rapidly and **6b**, was later removed from the column with methylene chloride. This separation gave an 80% crude yield of **6b** while the remaining products were not isolated but assessed by the integration of the appropriate *tert*-butyl peaks in the NMR spectrum of the fast-moving products. This indicated a 2% yield of **11** and a 7% yield of **12**.

Reduction of 1,4-Dimethyl-1,4-dihydro-2,4-diphenylquinazoline (4). A solution of 0.16 g (0.5 mmol) of **4** in 50 ml of THF was added to 0.3 g (8 mmol) of lithium aluminum hydride in 10 ml of THF. After 8 hr of reflux, the mixture was cooled and the excess hydride was destroyed with water, pentane was added, and the organic layer was decanted from the inorganic precipitate. Removal of the solvent gave the crude product, which was purified by preparative thin layer chromatography on silica gel using 1:1 benzene–petroleum ether as developing solvent. In order of increasing R_f, there were isolated 53 mg (33% recovery) of **4**, 13 mg of unidentified material, and 87 mg (55% yield) of **14** as an oil. The material was purified by recrystallization of the hydrochloride (decomposed above 138°) from benzene. The purified **14**, an oil, had NMR δ 1.75 (broad s, 1, NH, exchanges with D_2O), 1.90 (s, 3, CCH_3), 2.67 (s, 3, NCH_3), 3.32 and 3.55 (AB q, J = 12 Hz, 2, CH_2Ph), 6.67 (broad t, 2, aromatic H), 7.00 (s, 12, aromatic H); ir ($CHCl_3$) 3300 (NH), 1600, 1580, 1520, 1500, 1460, 1320, 1300, 700 cm^{-1}; mass spectrum *m/e* (rel intensity) 316 (M^+, 0.4), 301 (1), 239 (3), 211 (29), 210 (11), 209 (22), 208 (29), 194 (100), 165 (11), 106 (50), 91 (57), 77 (27).

Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.50; H, 7.65; N, 8.85. Found: C, 83.24; H, 7.82; N, 8.66.

Reduction of 1-Ethoxycarbonyl-4-methyl-2,4-diphenyl-1,4-dihydroquinazoline (13). The **13** was prepared by a modification of our earlier procedure.[5] After the reaction of methyllithium with **1**, the lithium salt was directly treated with ethyl chloroformate. This increased the yield of **13** to 79%. Spectral properties have been reported except for the mass spectrum: *m/e* (rel intensity) 370 (M^+, 2), 356 (28), 355 (100), 312 (11), 311 (45), 293 (20), 284 (10), 283 (46), 249 (19), 221 (22), 195 (10), 194 (65), 193 (10), 58 (11).

A solution of 0.75 g (2 mmol) of **13** in 25 ml of diethyl ether was added dropwise to a suspension of 0.3 g of lithium aluminum hydride in 100 ml of ether. After stirring at 20° for 18 hr and refluxing for 6 hr, the mixture was hydrolyzed with water and the ether layer decanted and evaporated. The residue (0.57 g) was treated with 20 ml of diethyl ether to give 0.23 g of **6**, mp 167–170°. The soluble portion was separated by preparative TLC on silica gel using 1:1 benzene–petroleum ether as developing solvent, giving as a fast-moving band 0.17 g (26% yield) of **14** and an additional 0.17 g of **6** (total yield 67%).

Repetition of the reduction in THF at 20° produced only **6**.

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Registry No.—**1**, 31730-65-1; **3**, 56844-90-7; **4**, 57256-03-8; **5**, 56844-85-0; **6a**, 56844-86-1; **6b**, 57256-04-9; **7**, 56844-91-8; **8**, 57256-05-0; **9**, 57256-06-1; **10**, 56869-71-7; **11**, 57256-07-2; **12**, 57256-08-3; **13**, 56844-89-4; **14**, 57256-09-4; lithium aluminum hydride, 16853-85-3; methyl iodide, 74-88-4; 1,3-dichloropropane, 142-28-9; 1,3-dibromopropane, 109-64-8; 1,3-diiodopropane, 627-31-6; 1,4-dibromobutane, 110-52-1; *tert*-butyl bromide, 507-19-7; ethyl chloroformate, 541-41-3; *tert*-butyllithium, 594-19-4.

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