acid chloride of 3-[(p-chlorophenyl)thio]-2,2-dimethylpropionic acid[1b] (see Experimental Section).
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(15) D. E. Heitmeier, J. T. Hortenstine, Jr., and A. P. Gray, *J. Org. Chem.*, **36**, 1449 (1971).
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(18) A. G. Cook, "Enamines: Synthesis, Structure, and Reactions", A. G. Cook, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 6.
(19) Isomer ratio of **11:12** is 4:1 (^{1}H NMR).
(20) H. Martin and R. Hirt, U.S. Patent 2,207,021.
(21) Data from 100-MHz spectrum performed and interpreted by S. A. Misak of The Upjohn Co.

Hydrogen and Alkyl Transfer in the Rearrangements of 2-Alkenyl-1,2-dihydroquinolines[1]

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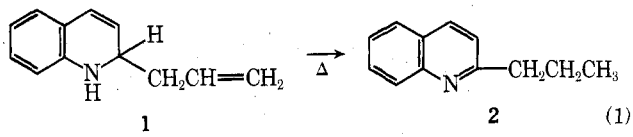
The addition of vinyl- or allylmagnesium chloride to quinoline yielded, at 25° and upon hydrolysis, the corresponding 2-alkenyl-1,2-dihydroquinoline. Heating the Grignard adduct with quinoline directly or heating the isolated dihydroquinoline caused isomerization to the corresponding 2-*n*-alkylquinoline or its magnesium salt, respectively. When the respective adducts were prepared from 2-deuterioquinoline and the subsequent isomerizations carried out, the resulting 2-*n*-alkylquinolines were found to be deuterated exclusively at the β position of the side chain. The coisomerization of 2-allyl-1,2-dihydroquinoline and 2-allyl-2,4-dideuterio-1,2-dihydroquinoline led to the production of much monodeuterated 2-*n*-propylquinoline, which indicates that such hydrogen transfer is largely, if not exclusively, intermolecular. 1,2-Dihydroquinolines and their N-metallic salts were found to undergo rather facile 1,2 elimination of RH or RM. In fact, 2-allyl-2-methyl-1,2-dihydroquinoline, as its *N*-magnesium chloride salt, was found to revert to quinaldine and allylmagnesium chloride. These components then recombined at higher temperatures to yield 4-allyl-2-methyl-1,4-dihydroquinoline as its *N*-magnesium salt. The foregoing findings point to two distinct pathways for intermolecular hydrogen transfer: (a) in the Grignard isomerization, a sequence involving MgHCl elimination, allyl–propenyl group isomerization, and 1,4 readdition of MgHCl; and (b) in the dihydro isomerization, elimination of RH in a free-radical initiation step, followed by concerted six-center hydrogen transfers and base-promoted allyl–propenyl group isomerization.

Hydrogen-transfer reactions of certain dihydropyridines have received much attention, since their conversion into pyridine derivatives is fundamental to the coenzymatic activity of dihydronicotinamide–adenine dinucleotide.[2] A special instance of this hydrogen transfer is that of isomerization, first observed in the rearrangement of 2-allyl-1,2-dihydroquinoline into 2-*n*-propylquinoline[3] (eq 1). Subse-



1 2 (1)

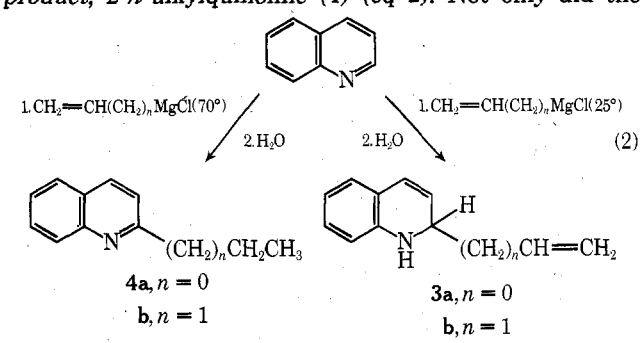
quently, isomerizing hydrogen transfers have been noted with similar derivatives, such as 4-allyl-1,4-dihydropyridines[4,5] and 2-phenylethynyl-1,2-dihydropyridine.[6]

In these isomerizations the dihydropyridinoid derivative acts, in a formal sense, both as a hydrogen donor and acceptor. As a consequence, a detailed study of the nature and scope of these rearrangements appeared to offer a unique opportunity for gaining a better understanding of hydrogen-transfer processes in these heterocycles.

The present report describes the preparation and rearrangement behavior of certain 2-alkenyl-1,2-dihydroquinolines, that bear a deuterium atom or a methyl group at C_2 and in which the alkenyl group is vinyl, allyl, and phenyl. The thermal and photochemical reactivity of these derivatives was examined in order to obtain information on (a) the nature of any intermediates; (b) the fate of any deuterium undergoing transfer; (c) the inter- or intramolecularity of the rearrangement; and (d) the nature of the reaction mechanism.

Results

The reaction of vinyl- or allylmagnesium chloride with quinoline yields the simple 1,2 adduct (**3**) at 25°, but prolonged heating favors the formation of the rearrangement product, 2-*n*-alkylquinoline (**4**) (eq 2). Not only did the

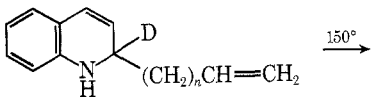


(2)

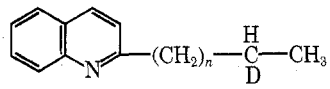
Grignard adducts themselves, namely the 2-alkenyl-1,2-dihydro-1-quinolylmagnesium chlorides, undergo rearrangement, but also the isolated, pure dihydro compounds, **3a** and **3b**, were found to isomerize into **4a** and **4b**, respectively, in 50–80% yields when heated under a nitrogen atmosphere above 130°. In addition, the irradiation at 254 nm of **3b** dissolved in benzene also caused isomerization into 2-*n*-propylquinoline (**4b**, 20% after 24 hr), but much deallylation with the formation of quinoline (60%) accompanied this process.

The fate of the NH and C_2H groups in **3** during the isomerization was studied by synthesizing C_2-deuterated analogs of **3a** and **3b** from 2-deuterioquinoline and the appropriate Grignard reagents (eq 2). Thermal rearrangement of

these compounds, **5a** and **5b**, yielded the respective 2-alkylquinolines, **6a** and **6b**, which by NMR spectroscopy were shown to be exclusively monodeuterated at the β carbon of the side chain (eq 3).



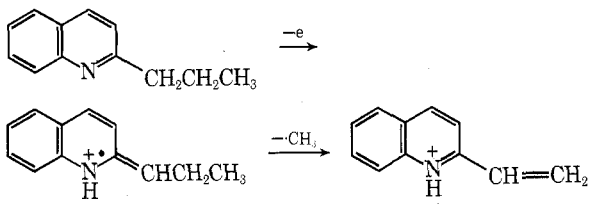
5a, $n = 0$
b, $n = 1$



(3)

6a, $n = 0$
b, $n = 1$

To test whether the hydrogen transfer takes place by an intramolecular or an intermolecular process, the thermal isomerization of a 1:1 mixture of 2-allyl-1,2-dihydroquinoline (**3b**) and 2-allyl-2,4-dideuterio-1,2-dihydroquinoline (**7**) was carried out at 150°. Mass spectral analysis of the crude reaction product, even at 20 eV, indicated the occurrence of much fragmentation and the presence of peaks corresponding to $C_{24}H_{22}N_2$ and $C_{24}H_{20}D_2N_2$ (338 and 340, respectively, presumably dimers of 2-propenylquinoline). Since fragmentation of the dimer contributed intensity to the P and P − 1 peaks of the 2-*n*-propylquinoline, the peaks in the mass range 170–173 could not be used for the detection of deuterium crossover. The P − 15 of **4b**, however, was found to be unchanged in intensity by the presence of such dimeric products (eq 4). The mass spectrum of



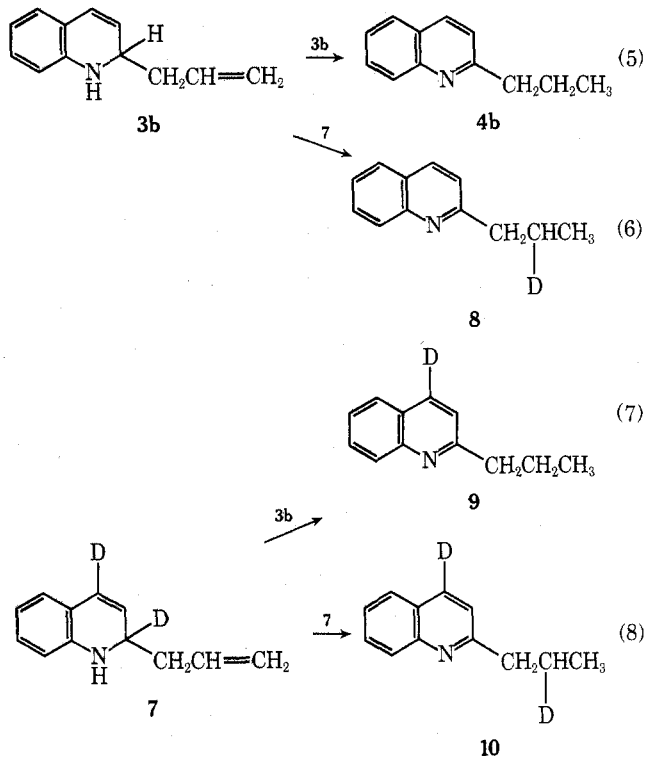
(4)

the crude 2-*n*-propylquinoline displayed peaks at *m/e* 158, 157, and 156 in a ratio of 1.2:1.2:1.0, respectively. The peak at *m/e* 157 can be ascribed to the presence of 2-*n*-(2-deuteriopropyl)- and 4-deuterio-2-*n*-propylquinolines (**8** and **9**), formed from the intermolecular hydrogen transfer between **3b** and **7** (Scheme I). Because a statistical intermolecular hydrogen transfer should result in the formation of **8** and **9** with the same probability as for **4b** and for **10**, the ratio of peaks at 158, 157, and 156 should be 1.0:2.0:1.0 for random exchange. On the other hand, exclusively intramolecular hydrogen transfer would lead to a ratio of 1.0:0:1.0. The observed ratio can mean either that both intramolecular and intermolecular hydrogen transfers are operative, or that a deuterium isotope ($k_H/k_D > 1.0$) favors the intermolecular reaction of 2-allyl-1,2-dihydroquinoline (**3b**) with itself. In this situation, as **3b** would be preferentially consumed in forming **4b**, the chances of **7** reacting with itself to form **10** would then increase.

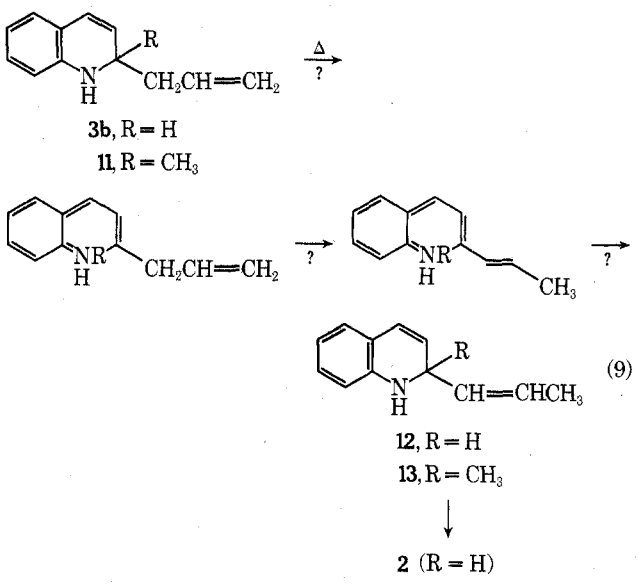
A mass spectral analysis of the 2-*n*-propylquinoline isolated by distillation from the coisomerization of **3b** and **7** showed the same ratio of peaks at *m/e* 158, 157, and 156.

Since 1,2-dihydroquinolines can be viewed as aza-substituted 1,3-cyclohexadienes, the question arose whether any part of the rearrangement involved an electrocyclic ring opening,[7] followed by an isomerization and an electrocyclic ring closure.[7] The final isomerization of the resulting 2-propenyl-1,2-dihydroquinoline (**12**) could be achieved by intermolecular hydrogen transfer (eq 9). If such electrocyclic processes were involved, then 2-allyl-2-methyl-1,2-dihydroquinoline (**11**), as the free base or the *N*-magnesium chloride salt (**14**), should be able to isomerize to **13**.

Scheme I

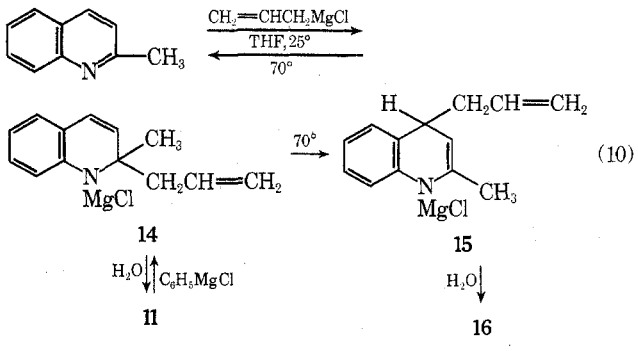


(5) (6) (7) (8)



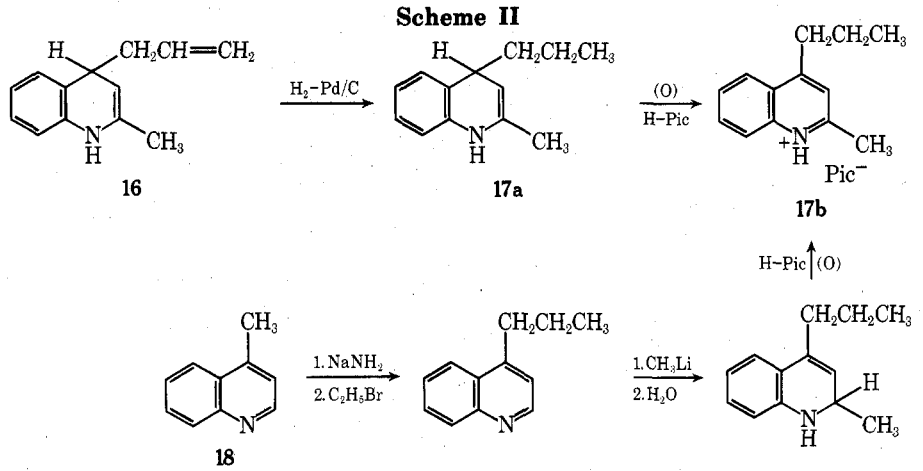
(9)

Therefore, **11** was prepared in high yield from the addition of allylmagnesium chloride in THF to 2-methylquinoline at 25°. Attempts to cause the isomerization envisaged



(10)

Scheme II

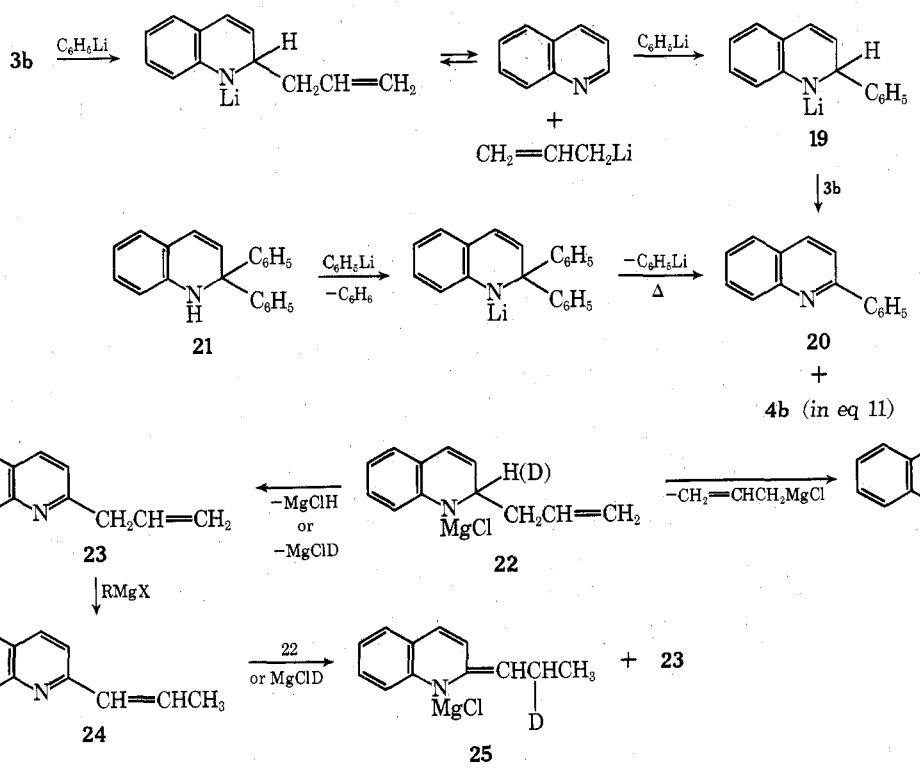


in eq 9, however, gave no discernible amount of **13**, but rather an allylic rearrangement. When the first-formed magnesium salt **14** was heated with an excess of Grignard reagent, the final principal product was the magnesium salt **15** of 4-allyl-2-methyl-1,4-dihydroquinoline (**16**) (eq 10). The proof of structure for **16** was achieved by means of spectroscopic data and by its catalytic hydrogenation to 2-methyl-4-*n*-propyl-1,4-dihydroquinoline (**17a**). The latter compound was oxidatively aromatized to 2-methyl-4-*n*-propylquinoline picrate (**17b**), which was identical in its spectral and physical properties with a sample synthesized unambiguously from lepidine (**18**)[8] (Scheme II).

Although the observed rearrangement of **14** into **15** effectively ruled out the occurrence of electrocyclic processes (eq 9) as part of the allyldihydro–propyl group isomerization (eq 10), the question as to the mechanism of the allyl group migration still remained. Either an intramolecular, [3,3] sigmatropic shift could be responsible[9] or the reelimination of allyl Grignard reagent from **14** to form quinaldine could occur, followed by the readdition of the Grignard reagent in a 1,4 manner. To test the tendency of **14** to undergo dissociation, **14** was prepared from pure, isolated **11** by treatment with phenylmagnesium chloride in THF. After 24 hr at room temperature such a solution was shown to contain 60% of quinaldine and 40% of **14**. Heating a solution of **14** at reflux led to 75% of quinaldine, 20% of **16**, and only 5% of **11**. From these results it is readily apparent that the dissociation of **14** is the dominant process in THF. Hence, **16** arises, most probably, from a thermodynamically controlled 1,4 Grignard addition to quinaldine.

This tendency of **14** to undergo elimination was found to be fairly general for such 2-substituted 1,2-dihydroquinolines. Thus, even treatment of **3b** with an excess of phenyllithium led to the isolation of 2-phenylquinoline (**20**), quinoline, and 2-*n*-propylquinoline. The products point to the dissociation of the lithium salt of **3b** into quinoline and allyllithium, the capture of some quinoline by phenyllithium, and the transfer of lithium hydride from **19** to **3b** yielding 2-phenylquinoline and 2-*n*-propylquinoline (eq 11). A phenyl group was found to be eliminated even from N-metallic salts of 2,2-diphenyl-1,2-dihydroquinoline (**21**), albeit such processes were slower (eq 12).

Not only did the metal salts of 1,2-dihydroquinolines tend to aromatize by loss of R–M, but the dihydro deriva-



tives themselves lost R–H at moderate temperatures or with photochemical activation. Heating 2-allyl-1,2-dihydroquinoline (**1**) under nitrogen gas above 130° always led to the formation of some quinoline and propylene, in addition to the usual isomerization to 2-*n*-propylquinoline (**2**) (eq 1). Indeed, direct heating of **1** at 285° gave almost equal parts of quinoline and **2**. Direct irradiation of **1** at 45° gave quinoline as the chief product. Likewise, the heating of **11** gave much quinaldine and propylene, together with complex rearrangement products.

These results on the thermal lability of dihydroquinolines and N-metallic salts show that during hydrogen-transfer (eq 1) and alkyl-transfer (eq 10) processes there are always varying amounts of the corresponding aza aromatic system present as a possible intermediate (quinoline in eq 1 and quinaldine in eq 10).

Discussion

The thermal rearrangements of 2-alkenyl-1,2-dihydroquinolines themselves (case I) and of their magnesium salts (case II) need not proceed by similar mechanisms. In fact, previous work on the interactions of organometallic reagents with the azomethine group would tend to support the operation of polar processes;[10] on the other hand, studies on the thermal decomposition of 1,2-dihydroquinolines have concluded that radical processes are involved.[11] Since kinetic studies on these rearrangements have not yet been made, the present discussion will consider what conclusions can be drawn from the foregoing product analyses. First of all, transfer of the C_2 H of 2-allyl-1,2-dihydroquinoline to yield 2-*n*-propylquinoline occurs largely, if not exclusively, intermolecularly. With the assumption of a modest isotope effect, $k_H/k_D \simeq 3$, and only one rate-limiting step, namely the formation of radical **31c**, the initial rate (ratio) of formation for **10**, **8** + **9**, and **4b** would be 1:4:3. A mixture of **3b** and **7** permitted to rearrange to completion should give a ratio of the peaks at *m/e* 158, 157, and 156 closer to 1:1:1, in general agreement with the observed ratio. However, more detailed work would be required to rule out any minor role for intramolecular transfer.

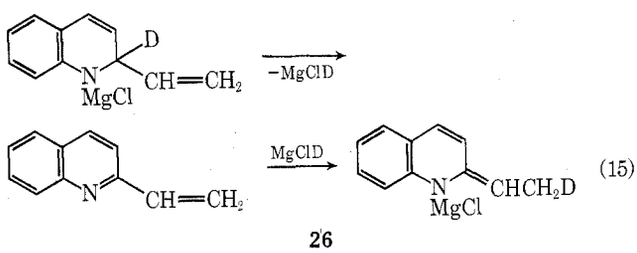
Secondly, the initiation of rearrangements in both cases would seem to occur by 1,2-elimination processes. For the N-metallic salts, it is well known that thermal elimination of metal hydrides leads to aromatization.[12] At higher temperatures metal alkyls have also been split out.[13] In this study the unusually ready elimination of allylmetallics and even the more difficult elimination of arylmetallics have been demonstrated. Likewise, for the 2-allyl-1,2-dihydroquinolines, **3b** and **11**, the facile elimination of propylene, presumably by a homolytic process, is remarkable. Quinoline is always produced in the isomerization of **3b**. From this known behavior, then, in the rearrangement of the magnesium salt **22**, it can be concluded that both quinoline and 2-allylquinoline (**22**) should be formed in small amounts (eq 13). The quinoline can be detected; the 2-allylquinoline has not been observed. However, it was previously established that Grignard reagents cause **23** to isomerize to **24**,[3a] and, in fact, small amounts of *trans*-2-propenylquinoline (**24**) have been detected in such Grignard isomerizations of **22**.

Thirdly, the actual isomerizations in both cases clearly involve intermolecular hydrogen transfers. In the Grignard process, such attack would seem to be the polar attack of MgClH (MgClD) or **22** on **24**, with formation of **25** and the generation of more **23** (when **22** is source of MgClH) (eq 14). A cyclic process

$$23 \longrightarrow 24 \xrightarrow{22} 25 + 23$$

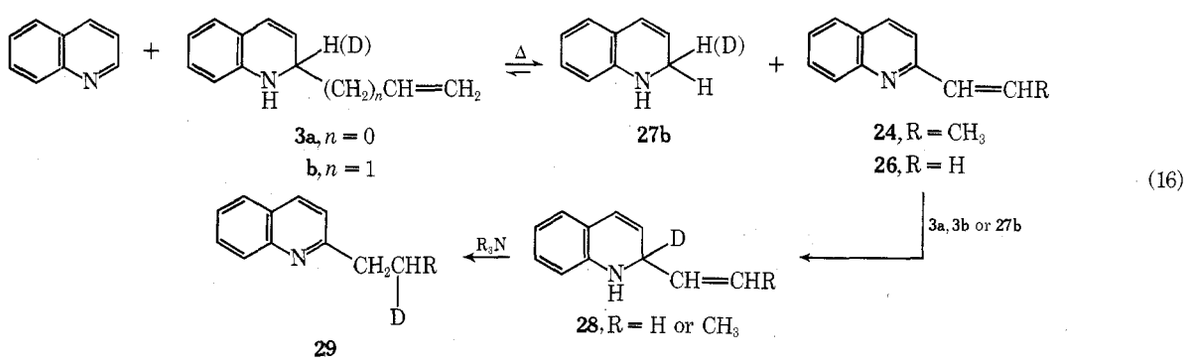
could thus perpetuate the conversion to 2-*n*-propylquinoline. Whether **22** is the source of hydride by elimination (→ **23**) or direct transfer (**24** → **25**) is unclear; in any event, the C_2 D is correctly predicted to enter the β position of the propyl side chain (**25**).

This mechanistic pathway can readily account for the Grignard isomerization of 2-vinyl-1,2-dihydroquinoline (**3a**), except that here no prototropic shift (**23** → **24**) is involved (eq 15).



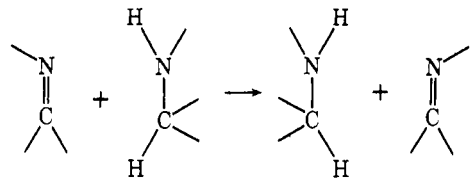
(15)

With the direct isomerization of 2-alkenyl-1,2-dihydroquinolines, thermal equilibration with the quinoline produced by 1,2 elimination could lead to the formation of 1,2-dihydroquinoline and 2-alkenylquinoline (**23**, **24**, or **26**). These alkenyl intermediates could then undergo reduction via hydrogen transfer from **3a** or **3b** (or **27b**), respectively (eq 16). The transfers of HD from **3a** or **3b** to quinoline to yield **27b** and from **3a**, **3b**, or **27b** to **24** or **26** to yield **28** may not be concerted, but such concerted double group transfers would be expected to be thermally allowed.[14] On the other hand, interaction of **24** or **26** with **3** or **27b** to yield **29** directly would not be a thermally allowed, concerted process (eq 17). Hence, thermally allowed transfers and a final base-catalyzed isomerization of **28** into **29** are proposed. Again, the position of C_2 D in **3** at the β position in **29** is consistent with these pathways.



(16)

Finally, in the absence of kinetic results, the question of radical-induced initiation steps in these rearrangements must be left open. Just as there is evidence for single electron transfer in Grignard additions to carbonyl and azo-



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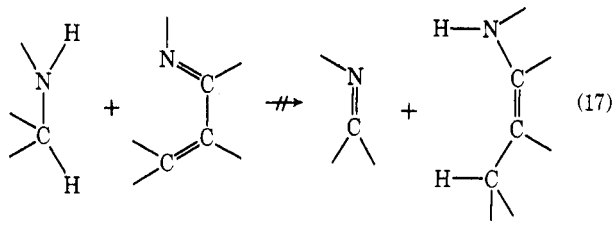
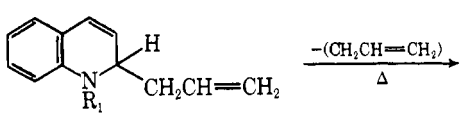
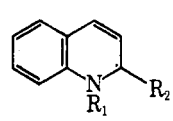


(17)

methine linkages,[15] so the reversal of these additions might involve homolysis (**30a** → **31a**). Such rupture may be related to the probable homolysis encountered with the 2-allyl-1,2-dihydroquinolines themselves (**30b** → **31b**). These stabilized 1-substituted dihydroquinolyl radicals might then initiate free-radical, hydrogen-transfer chains. The occurrence of a radical process in these isomerizations is consistent with the observed formation of dimeric and polymeric by-products. However, if radical chains were to be operative in the actual hydrogen-transfer steps, such chains would have to achieve the specific transfer of the C_2 D in **3** and **22** to the β position of the resulting alkylquinoline.



30a, R_1 = MgCl
b, R_1 = H



31a, R_1 = MgCl; R_2 = H
b, R_1, R_2 = H
c, R_1 = H; R_2 = $CH_2CH{=}CH_2$

Experimental Section

All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra (ir) were recorded on a Perkin-Elmer spectrometer, Model 137, equipped with sodium chloride optics. Proton magnetic resonance spectra (^{1}H NMR) were obtained with a Varian spectrometer, Model A-60, on neat samples or on 10% solutions in pure solvents. The values are reported on the δ scale in parts per million with reference to internal or external tetramethylsilane, followed by the relative proton intensities and the coupling constants (J) in hertz. Vapor phase chromatographic analysis (VPC) and isolations were carried out on an F & M chromatograph, Model 720, equipped with a 6 ft × 0.25 in. column of 10% SE-30 silicone gum rubber on Chromosorb P. Mass spectra of solids and liquids were obtained on a Varian MAT spectrometer, Model CH5, and those of gases on a Consolidated Electrodynamics instrument, Model CEC-21-620A. Elemental analyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Mich.

All preparations and reactions involving air- and moisture-sensitive organometallic or heterocyclic intermediates were conducted under an atmosphere of dry, oxygen-free nitrogen, with adherence to published procedures.[16] Solvents of reagent grade were used in all reactions. The anhydrous ethyl ether (Fisher) was used directly; the tetrahydrofuran and benzene were dried just before use by distilling them from the sodium ketyl of benzophenone under a dry nitrogen atmosphere.

Photochemical reactions were run in a Rayonet apparatus, Model 100, equipped with low-pressure mercury (254 nm) lamps.

Preparation of Starting Materials. Allylmagnesium bromide in ethyl ether,[17] allylmagnesium chloride in tetrahydrofuran,[18] allyllithium in ethyl ether,[19] vinylmagnesium chloride in tetrahydrofuran,[20] and n-butyllithium in ethyl ether[21] were prepared according to published procedures. n-Butyllithium in hexane was from the Foote Mineral Co.

2-Bromoquinoline was prepared from carbostyril and $POBr_3$ to yield colorless crystals from 95% ethanol, mp 47.5–49° (lit.[22] mp 47–49°). 2-Phenylquinoline was obtained from quinoline and phenyllithium, mp 81–82.5° (lit.[23] mp 83–84°).

2-Deuterioquinoline was prepared from 2-chloroquinoline by reduction with powdered tin metal in the presence of deuterium oxide (99.8% D).[24] By mass spectrometric measurement of the m/e 130 peak and by the absence of the C_2 H peak in the NMR spectrum, the product was found to be >99% pure.

2,2-Diphenyl-1,2-dihydroquinoline was prepared from 2-phenylquinoline and phenyllithium, according to a published procedure.[25] Repeated recrystallizations of the crude distilled product from ethanol gave a colorless solid, mp 95–97°. Since this melting point was considerably higher than the reported value of 86–87°, spectral data were examined: ir (CCl_4) 3450 cm^{-1} (N–H); NMR (CCl_4) δ 4.0 (broad s, NH), 5.8–6.9 (m, 6 H), and 7.3 (broad s, 10 H); MS P m/e 283. Apparently, the previously reported product was contaminated with 2-phenylquinoline.

2,4-Dichloroquinoline. Admixture of 80.0 g (0.39 mol) of the disodium salt of 2,4-dihydroxyquinoline (Pfaltz and Bauer) with 250 g (1.2 mol) of phosphorus pentachloride was conducted slowly, while cooling in an ice bath, since the components reacted vigorously. After 15 min 290 g (1.9 mol) of phosphorus oxychloride were added dropwise to the aforementioned chilled and stirred mixture. The resulting brown mixture was stirred at 100° for 3 hr, then cooled in an ice bath and finally poured slowly into ice water (*caution*). The thawed, yellow solution was made slightly basic by the addition of concentrated, aqueous NaOH solution. Extraction of this solution with ether, drying of the extracts over anhydrous Na_2SO_4, removal of the solvent, and distillation gave 46.4 g (60%) of crude 2,4-dichloroquinoline, bp 112–114° (0.70 mm). Recrystallization of the solidified distillate from methanol provided a 50% yield of colorless crystals, mp 61–63° (lit.[26] mp 66–67°).

2,4-Dideuterioquinoline. A mixture of 15.0 g (0.076 mol) of 2,4-dichloroquinoline, 24.0 g (0.20 g-atom) of tin metal (powdered to pass 240 mesh screen), and 150 ml of deuterium oxide (99.8% D) was heated at 70° for 15 min under a nitrogen atmosphere. Then 48.0 g (0.313 mol) of phosphorus oxychloride was added dropwise to the vigorously stirred mixture, during which the grayish-brown mixture became a pinkish yellow. After 6 hr of stirring at 70–75° and 3 hr at 25° the mixture was cooled in an ice bath and slowly basified with aqueous NaOH solution. Ether extraction of the basic mixture, drying of the extracts over anhydrous Na_2SO_4, removal of the solvent, and distillation gave a 57% yield of 2,4-dideuterioquinoline bp 58–61° (0.35 mm). Spectral data: ir (neat) 3280 and 3070 (C–H stretch), 2275 (C–D stretch), 1640 and 1570 (C=C stretch), 1400, 1085, 918, 905, and 770 cm^{-1}; NMR (CCl_4) δ 7.17 (broad s, 1 H), 7.3–7.8 (m, 3 H), 8.05–8.30 (m, 1 H) and no traces of C_2 H or C_4 H; MS m/e (rel intensity) 132 (14), 131 (P, 100), 130 (18), 129 (11), 104 (18), 103 (21), and 76 (14). The compound was greater than 98% dideuterated.

4-n-Propylquinoline. Under a nitrogen atmosphere, a solution of 11.2 g (78 mmol) of 4-methylquinoline in 100 ml of anhydrous ethyl ether was cooled in a bath and then, with stirring, a slurry of sodium amide (10.0 g, 0.256 mol) in 100 ml of ethyl ether was gradually introduced. The greenish-blue solution was stirred at 25–30° for 4 hr and again cooled in an ice bath. A color change to a blue-brown was noted as an ethereal solution of ethyl bromide (9.0 g, 83 mmol) was added dropwise. After 2.5 hr at room temperature the cooled mixture was cautiously hydrolyzed with water. The ethereal layer was separated, washed with water until weakly basic, dried with anhydrous Na_2SO_4, and free of solvent. The residual yellow oil (11.2 g) was shown by NMR spectroscopy to consist of 4-n-propylquinoline (56%), 4-(3-pentyl)quinoline (31%), and 4-methylquinoline (13%). Fractional distillation through a 10 × 1 cm column filled with glass helices eventually gave pure 4-n-propylquinoline: bp 110–111° (1.35 mm); NMR (CCl_4) δ 0.83 (t, CH_3, J = 7.0 Hz), 1.55 (unsymmetrical sextet, CH_2), 2.78 (t, CH_3, J = 7.5 Hz), 6.9–8.3 (m, 5 H), and 8.66–8.9 (m, 1 H); picrate, yellow needles, mp 204–204.5° (lit.[8] mp 204°, 207°). The 4-(3-pentyl)quinoline gave a

picrate as yellow needles, mp 133–133.5°, and displayed NMR signals in CCl_4 at δ 0.72 (t, CH_3, J = 7.0 Hz), 1.71 (q, CH_2), and 2.75–3.3 (m, CH).

2-Methyl-4-*n*-propylquinoline. A solution of 2.5 g (15 mmol) of 4-*n*-propylquinoline in 100 ml of anhydrous ethyl ether was treated dropwise at 0° with 125 ml of an ethereal methyllithium solution (48 mmol). After 24 hr at 20–25° the resulting dark green solution was treated with water and the ethereal layer separated. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and freed of solvent. The residual oil was heated at reflux with 15 g of nitrobenzene for 3 hr. The cooled solution was made acidic by adding 150 ml of 10% aqueous hydrochloric acid and the insoluble nitrobenzene and other products were then extracted into ether. The aqueous layer was then basified with 20% potassium hydroxide solution and the liberated oil was taken up in ether. Usual work-up of the ether extract gave an 89% yield of the crude 2-methyl-4-*n*-propylquinoline. Purification through the picrate (mp 199–201° from ethanol) gave the pure product. Spectral data on the quinoline: ir (neat) 3075, 2985, 2880, 1615, 1575, 1370, 1195, 1025, 872, and 762 cm^{-1}; NMR (CCl_4) δ 0.75–1.15 (t, 3 H), 1.5–1.9 (broad m, 2 H), 2.65 (s, 3 H), 2.5–3.0 (broad m, 2 H), and 6.4–8.1 (m, 5 H); MS *m/e* (rel intensity) 185 (P, 100), 170 (39), 157 (72), 156 (78), 142 (12), 129 (21), 128 (25), and 115 (50). Spectral data on the picrate: MS *m/e* (rel intensity) 228 (22), 185 (100), 170 (39), 157 (69), 156 (69), 142 (7), 129 (19), 128 (22), and 115 (42).

Anal. Calcd. for $C_{19}H_{18}N_4O_7$: C, 55.07; H, 4.38; N, 13.52. Found: C, 55.09; H, 4.32; N, 13.46.

2-Allyl-1,2-dihydroquinoline (3b). With adherence to the published procedure,[3a] this compound was prepared from quinoline and allylmagnesium bromide in tetrahydrofuran solution. The highest yields of pure product, which contained very little 2-*n*-propylquinoline, were obtained when the hydrolytic work-up and distillative isolation were done promptly and under an atmosphere of nitrogen. Especially important was that the 10 × 1 cm, glass helices filled fractionating column was wrapped with an electrically heated tape, so that overheating of the distillate and a prolonged residence time in the column did not occur. Spectral data: ir (neat) 3390 (N–H stretch), 3030, 2860, 1645 (C=CH_2 stretch), 1480, 1315, 1120, 995, and 915 cm^{-1} (CH=CH_2); NMR (CCl_4) δ 2.0 (t, 2 H, J = 6.5 Hz), 3.5 (broad s, 1 H), 3.9 broad m, 1 H), 4.6–5.8 (m, 4 H), and 6.0–6.8 (m, 5 H).

2-Allyl-2-deuterio-1,2-dihydroquinoline (5b). This compound was prepared in 67% yield from 0.12 mol of 2-deuterioquinoline by use of the published procedure. Its ir spectrum showed a band at 2105 cm^{-1} (C–D stretch) and its NMR spectrum lacked the broad multiplet centered at 3.9 ppm (C_2 H) and displayed only a doublet at 2.0 ppm (J = 6.5 Hz).

2-Allyl-2,4-dideuterio-1,2-dihydroquinoline (7). This compound was isolated pure in 60% yield by applying the foregoing alkylation procedure to 46 mmol of 2,4-dideuterioquinoline. Its ir spectrum showed a C–D stretch at 2250 cm^{-1} and its NMR spectrum (CCl_4) had a doublet at 2.0 ppm ($DCCH_2CH=CH_2$), but lacked the broad multiplet at 3.9 ppm (C_2 H) and had over four protons in the 6.0–6.8 ppm region.

Reaction of 2-Methylquinoline with Allylmagnesium Chloride at 25°. 2-Allyl-2-methyl-1,2-dihydroquinoline (11). A chilled solution of allylmagnesium chloride (0.375 mol) in 300 ml of tetrahydrofuran was added dropwise to a solution of 2-methylquinoline (18.0 g, 0.126 mol) in 180 ml of tetrahydrofuran, which was maintained at 0°. A yellow-green color developed immediately upon admixing the reagents and deepened to dark green during the 20-hr reaction period at 20–25°. The reaction mixture was cooled in an ice bath, hydrolyzed with saturated aqueous NH_4Cl solution, and treated with ethyl ether. (All work-up procedures were performed under a nitrogen atmosphere.) The organic layer was separated, washed with water, dried with anhydrous $CaSO_4$, and freed from solvent. By NMR spectroscopic comparison of the methyl signal intensities at 2.6 (2-methylquinoline) and 1.2 ppm (the 2-allyl-2-methyl-1,2-dihydro product), the reaction was found to have given a yield of ca. 95%.

Distillation through a 10 × 1 cm, glass helices filled column, which was wrapped and warmed with electrical heating tape, provided 2-allyl-2-methyl-1,2-dihydroquinoline as a yellow liquid: bp 82–83° (0.28 mm); ir (neat) 3425 (N–H stretch), 1655 (s, C=C), 1625 (s, aromatic stretch), 1590 (conjugated C=C), 915 and 995 cm^{-1} (C–H deformations of CH=CH_2); NMR (CCl_4) δ 1.17 (s, CH_3), 2.1–2.3 (d, 2 H, J = 7.0 Hz), 3.58 (br s, NH), 4.85–6.0 (m, 4 H, CH=CH_2 and C_3 H), and 6.1–7.1 (m, 5 H).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.30; H, 8.16; N, 7.45.

Reactions of Quinoline with Vinylmagnesium Chloride. A solution of 46.6 g (0.361 mol) of quinoline in 130 ml of dry tetrahydrofuran was admixed at 0° with 0.481 mol of vinylmagnesium chloride in 200 ml of tetrahydrofuran, whereupon a dark yellow-brown color developed. After 24 hr at 20–25° the solution was hydrolyzed with aqueous NH_4Cl solution and then worked up under a nitrogen atmosphere, as in the foregoing procedure. Combined NMR and ir spectral analyses of the resulting oil (45 g) indicated the presence of <5% of quinoline [NMR (CCl_4) no discernible, characteristic q for C_2 H at 8.6–8.7 ppm, but ir (neat) weak bands at 830 and 805 cm^{-1}], 70% of 2-vinyl-1,2-dihydroquinoline [ir (neat) 3390 (N–H stretch) and 995 and 915 cm^{-1} (C–H deformations of CH=CH_2); NMR (CCl_4, external Me_4Si) δ 3.97 (br s, NH), 4.52 (br t, C_2 H), 4.68–5.08 (m, CH=CH_2), 5.26 (d of d, C_3 H, $J_{3,4}$ = 9.0, $J_{2,4}$ = 4.0 Hz), 5.81 (m, CH=CH), 6.1 (d, C_4 H, $J_{3,4}$ = 9.0 Hz), and 6.0–7.0 (m)], and 30% of 2-ethylquinoline [NMR (CCl_4) 1.32 (t, CH_3, J = 7.5 Hz), 2.91 (q, CH_3, J = 7.5 Hz), and 6.95–8.2 (m)]. Attempts to separate these major components by fractional distillation were unsuccessful. Prolonged heating led to polymerization, some cracking to quinoline [NMR (CCl_4) 8.6–8.7 ppm], some oxidation to 2-vinylquinoline [NMR (CCl_4) 6.1 (m, CH=CH_2) and 5.22 ppm [d of d, distinct from the 2-vinyl-1,2-dihydro derivative, CH=CH (trans)]], and gradual isomerization into 2-ethylquinoline: bp (51–52° (0.04 mm); ir (neat) 3080, 2990, 1615, 1520, 1435, 1305, 1125, 950, and 835 cm^{-1}; picrate mp 147–148° (lit.[27] mp 148°).

Reaction of 2-Deuterioquinoline with Vinylmagnesium Chloride. As in the foregoing procedure, 2-deuterioquinoline (13.0 g, 0.10 mol) was allowed to react with 0.102 mol of the Grignard reagent in tetrahydrofuran at 20–25° for 24 hr. The usual hydrolytic work-up under a nitrogen atmosphere and solvent removal gave a yellow oil whose NMR spectrum (CCl_4) showed only traces of quinoline and 2-ethylquinoline: δ 3.63 (br s, NH), 4.55–4.92 (m, CH=CH_2), 5.13 (d, CH=CH_2, $J_{3,4}$ = 9.0 Hz), 5.53 (d of d, CH=CH, J_{trans} = 15 and J_{cis} = 9 Hz), 5.95 (d, C_4 H, $J_{3,4}$ = 9.0 Hz), and 5.75–6.70 (m). Only weak triplets of the deuterated 2-ethylquinoline were observed at 1.3 and 2.85 ppm, and the C_2 H of 2-vinyl-1,2-dihydroquinoline at 4.5 ppm was absent. Thus, the product consisted of >90% 2-deuterio-2-vinyl-1,2-dihydroquinoline.

Since fractional distillation caused isomerization to the ethylquinoline, the whole product was heated at 148–150° under nitrogen for 48 hr. The NMR spectrum of the crude product (CCl_4) was principally that of 2-(2-deuterioethyl)quinoline. Fractional distillation gave the product contaminated with ca. 10% deuterated quinoline and other impurities: bp 58–59° (0.15 mm); NMR (CCl_4) δ 1.25 (t ot t, CH_2D, J = 7.5, J_{HD} = 1.2 Hz), 2.80 (t, CH_2), ratio of CH_2D/CH_2 1:1, 6.75–7.9 (m), with trace absorptions at δ 1.7, 2.5, 3.9, and 6.0–6.7.

Reaction of 2-Allyl-1,2-dihydroquinoline with Phenyllithium. To a solution of 3.75 g (0.023 mol) of freshly distilled 2-allyl-1,2-dihydroquinoline in 50 ml of benzene was added 40 ml (0.049 mol) of a 1.25 *N* ethereal phenyllithium solution. The solution became dark red and a yellow precipitate was formed during the addition. The solution was heated under reflux for 90 min, cooled, and then hydrolyzed with water. After the usual work-up and removal of solvent, the organic residue was distilled to yield two principal fractions: (1) bp 80–95° (0.4 mm), containing principally quinoline and 2-*n*-propylquinoline [ir (neat) 815 and 835 cm^{-1}]; and (2) bp 95–120° (0.4 mm), a waxy, pale yellow solid, 1.5 g. The latter solid was chromatographed on a 90 × 2.5 cm column of neutral alumina and the components were eluted with petroleum ether (bp 30–60°). The principal component was 2-phenylquinoline, mp 80–82° (lit.[23] mp 81–83°), picrate (EtOH) mp 190–191.5° (lit. mp 191°).

Reaction of 2,2-Diphenyl-1,2-dihydroquinoline with Phenyllithium. A solution of 2.0 g (7 mmol) of the diphenyl-1,2-dihydro compound in 100 ml of dry benzene was treated with 30 ml of a 0.65 *N* ethereal solution of phenyllithium (20 mmol). The resulting bright yellow solution was heated at reflux for 80 hr and then hydrolyzed. Work-up gave an organic oil that was chromatographed on a 64 × 3 cm column of silica gel and the components were eluted by a sequence of hexane, hexane–benzene, and benzene–ether. The principal component isolated was 2-phenylquinoline, as demonstrated by spectral and melting point comparisons.

Reaction of 2-Allyl-2-methyl-1,2-dihydroquinoline with Phenylmagnesium Chloride. To a solution of 4.5 g (24.4 mmol) of the freshly distilled and pure dihydroquinoline in 40 ml of dry tetrahydrofuran was added 100 ml of 0.48 *N* phenylmagnesium chloride in the same solvent. Gradually the resulting solution became yellow-green during 24 hr at 20–25°. One-half of the solution

was then withdrawn and hydrolyzed with an aqueous NH_4Cl solution. The organic layer was diluted with ethyl ether, separated, washed with water, dried over anhydrous Mg_2SO_4, and then freed of solvent in vacuo. The resulting oil (2.5 g) was shown by NMR spectroscopy to consist of 60% 2-methylquinoline and 40% 2-allyl-2-methyl-1,2-dihydroquinoline.

The remaining portion of the original reaction mixture was heated at reflux under a nitrogen atmosphere for 24 hr. The resulting brown solution was hydrolyzed and worked up as described above. The dark brown oil (2.3 g) was shown by NMR spectroscopy to consist of 75% 2-methylquinoline, 20% 4-allyl-2-methyl-1,4-dihydroquinoline (cf. infra), and only ca. 5% 2-allyl-2-methyl-1,2-dihydroquinoline.

Reaction of 2-Methylquinoline with Allylmagnesium Chloride at 70°. 4-Allyl-2-methyl-1,4-dihydroquinoline (16). A solution of 23.0 g (0.161 mol) of 2-methylquinoline in 120 ml of dry tetrahydrofuran was allowed to react with 270 ml (0.392 mol) of 1.45 *N* allylmagnesium chloride in tetrahydrofuran for a period of 20 hr at 20–25° and 25 hr at reflux. The usual hydrolytic work-up yielded a brown oil (29.8 g), whose NMR spectrum had only weak signals characteristic of 2-allyl-2-methyl-1,2-dihydroquinoline (especially at 1.17 ppm) and perhaps small amounts of 2-methylquinoline. The principal absorptions were multiplets of moderate intensity at 1.0–1.4, 2.4–2.8, and 3.2–3.7 ppm, as well as intense bands at 2.10 (s), 2.15–2.4 (m), 4.7–5.1 (m, CH_2=CH), 5.1–5.9 (m), and 6.2–7.2 ppm (m). Fractional distillation at 0.4 mmHg pressure yielded four fractions: (1) bp 86–90°; (2) bp 91–94°; (3) bp 95–99°; and (4) bp 102–130°. The NMR and ir spectra of fractions 1–3 were very similar: aside from minor differences in the region of 1.0–1.5 ppm, these spectra exhibited signals consistent with the presence of allylmethyldihydroquinoline derivatives [ir 3280 (N–H), 1630 (C=C), 995, and 915 cm^{-1}]. Although the NMR spectrum was complex, the presence of the following components seemed to be evident: (1) 4-allyl-2-methyl-1,4-dihydroquinoline as the principal component (ca. 75%) [2.07 (s, CH_3), 1.95–2.35 (m, CH_2CH=CH_2), 3.1–3.4 ppm (m, C_4 H)] (cf. infra for structure proof); (2) 4-allyl-2-methylquinoline [2.60 (s, CH_3), 3.68 ppm (d, CH_2)]; and (3) 4-allyl-2-methyl-1,2-dihydroquinoline [1.1 ppm (d, CH_3)].

Fraction 4 had quite different NMR and ir spectra, displaying as principal absorptions those signals found in the other fractions as minor bands. As will be seen, these bands were best attributable to tetrahydroquinoline derivatives.

In order to aid the identification of these components, a 6.0-g portion of fraction 3 dissolved in 125 ml of absolute ethanol was hydrogenated at 20–25° under 1 atm in the presence of 0.3 g of a catalyst of 10% palladium on charcoal. After 27 hr the amount of hydrogen necessary to reduce one C=C bond had been absorbed. The filtered ethanolic reaction solution was treated with picric acid: mp 198–200°; the mixture melting point with an authentic sample of 2-methyl-4-*n*-propylquinoline picrate was undepressed, and the NMR and ir spectra were superimposable.

The ethanolic filtrate from the picrate preparation was made basic with 10% aqueous KOH solution and the liberated oil was taken up in ether. Drying over anhydrous Na_2SO_4 and removal of solvent in vacuo gave a brown oil: ir (neat) 3380 cm^{-1} (N–H) but no C=C or CH=CH_2 bands; NMR (CCl_4) δ 0.8–2.1 (m, 15 H), 2.4–3.6 (m, 4 H), and 6.2–7.1 (4 H); mass spectrum *m/e* (rel intensity) 189 (P, 54), 185 (8), 174 (59), 146 (100), 144 (27), 132 (15), 130 (16), and 118 (10). These data permit the conclusion that this oil is a mixture of 2-methyl-4-*n*-propyl-1,2,3,4-tetrahydroquinolines.

Thermal Rearrangement of 2-Allyl-1,2-dihydroquinoline. A. General Procedure. A freshly distilled sample (4.0–8.0 g, 23–46 mmol) that had been purified under nitrogen and analyzed by NMR spectroscopy was placed in a 25-ml, pear-shaped flask connected to an air-reflux condenser. The top of the condenser was connected both to the nitrogen line and to a vacuum line by means of a three-way stopcock. By chilling the sample flask in a solid CO_2–acetone bath and by the alternate application of reduced pressure and nitrogen, all traces of moisture and oxygen were minimized. The system was then opened to a gas manifold at atmosphere pressure, which manifold led through a trap at −78° to a closed, evacuated gas collection bulb. After the heating period had ended, the liquid in the cold trap was allowed to evaporate into the gas collection bulb, by lowering the cooling bath from the trap and opening the stopcock on the collection bulb. The gas was analyzed by mass spectrometry and the liquid residue in the pyrolysis flask separated by distillation and examined by ir and NMR spectroscopy, as well as mass spectroscopy.

From the results of 15 different pyrolyses conducted variously at temperatures between 130 and 300° and at times of 1–72 hr, with samples of different purity, the following conclusion can be drawn. First of all, the purest samples yield 2-*n*-propylquinoline, quinoline, propylene, and small amounts of *trans*-2-propenylquinoline and its dimer. The propylene was identified as the principal volatile component by its MS (70 eV) prominent peaks at *m/e* 42, 41, 27, and 15. Fractional distillation of the liquid product permitted the ready isolation of quinoline; even in the crude liquid, its presence was easily discerned by its NMR quartet at 8.6–8.7 ppm for its C_2 H and its ir bands at 805 and 830 cm^{-1}. The 2-*n*-propylquinoline was essentially pure after distillation: bp 85–87° (0.1 mm); ir (neat) prominent bands at 3030, 2945, 1600, 1505, 1565, 1420, 1305, 1115, 1045, and 828 cm^{-1}; NMR CCl_4) δ 0.97 (t, CH_3, J = 7.2 Hz), 1.83 (br sextet, CH_2), 2.88 (br t, CH_2, J = 7.0 Hz), 7.04 (d, C_3 H, J = 8.5 Hz), 7.25–8.1 (m, 5 H); picrate, yellow needles from EtOH, mp 162.5–163.5° (lit.[3a] mp 163–164°); mixture melting point undepressed. Traces of *trans*-2-propenylquinoline in such distillates were detected by the presence of a characteristic ir band at 970 cm^{-1}. In the mass spectrum of the distillation residue distillation residue peaks were observed at *m/e* (rel intensity) 340 (8), 339 (12), 338 (25), 324 (8), 323 (21), 200 (8), 199 (17), 198 (100), and 196 (27). These data are consistent with the presence of a dimer (or higher oligomer) of 2-propenylquinoline (mol wt 340) and its principal cracking by loss of the quinaldinyl group (P − 142).

The second conclusion on these pyrolysis is that higher temperatures favor the formation of propylene and quinoline (temperature and percent of quinoline): 130–140°, trace; 160–170°, 2%; and 285°, 52%.

Thirdly, starting material that was stored under nitrogen for several weeks before pyrolysis gave a significantly higher proportion of *trans*-2-propenylquinoline and gummy products (25–35%).

Fourthly, the cleanest isomerization was achieved by heating a 4.0-g sample of pure 2-allyl-1,2-dihydroquinoline in a Wood's metal bath for 10–20 hr at 150–165°. Only about 2% of quinoline was formed; the distillate was pure 2-*n*-propylquinoline.

B. Pyrolysis of 2-Allyl-2-deuterio-1,2-dihydroquinoline. A 5.4-g sample (31 mmol) was heated at 150–155° for 24 hr under a nitrogen atmosphere. Since an NMR spectrum showed the presence of some starting material, the liquid was heated for an additional 24 hr. Fractional distillation of the product gave essentially pure 2-(2-deuterio-*n*-propyl)quinoline containing traces of quinoline: bp 80–82° (0.1 mm); ir (neat) 3040, 2900, 2155 (C–D stretch), 1600, 1505, 1425, 1305, 1115, and 828 cm^{-1}; NMR (CCl_4) δ 0.97 (d, 3 H), 1.5–1.9 (complex m, 1 H), 2.88 (d, 2 H), and 6.8–7.9 (m, 6 H).

When a sample of the starting material was heated at 150° for 24 hr, the gas evolved was shown by MS to be essentially, if not all, undeuterated propylene.

C. Crossover Experiment between 2-Allyl-1,2-dihydroquinoline and 2-Allyl-2,4-dideuterio-1,2-dihydroquinoline. In three different sample tubes were placed, respectively, 3.0 g (16 mmol) of 2-allyl-2,4-dideuterio-1,2-dihydroquinoline (sample A), 3.0 g (16 mmol) of its undeuterated counterpart (sample B), and finallly a mixture of 1.5 g each of these two components (sample C). All three sample flasks were heated, under nitrogen, in the same oil bath for 40 hr at 148–150°. Then each sample was submitted directly to spectral and mass spectrometric analyses.

Sample A: by ir and NMR analyses the principal product was shown to be 2-(2-deuterio-*n*-propyl)-4-deuterioquinoline (ca. 96%), with only 4% of starting allyldihydro compound remaining: ir (neat) 3490 (weak N–H stretch), 2275 and 2178 (C–D stretches); NMR (CCl_4) δ 0.98 (d, 3 H), 1.5–1.9 (complex m, 1 H), 2.88 (d, 2 H), and 7.0–8.1 (m, 5 H). Any 2-deuterioquinoline present would not have been observable.

Sample B: by the spectral criteria given above, this product was found to contain 91% 2-*n*-propylquinoline, 6% quinoline, and 3% starting allyldihydro compound.

Sample C: this contained 88% 2-*n*-propylquinoline (in deuterated and undeuterated forms), 4% quinoline (deuterated not included), and the balance as allyldihydro compounds.

The mass spectra of these crude samples, even at a low ionization voltage of 20 eV, proved to be somewhat less suitable for detection of crossover, because of the presence of considerable amounts of components of higher molecular weight, such as the 2-propenylquinoline dimers mentioned above. Cracking of these dimers contributed to the parent and P − 1 peaks of deuterated and undeuterated 2-*n*-propylquinolines, *m/e* 173, 172, 171, and 170, thus vitiating any conclusions about crossover that might be based

on the *m/e* 172 peak. However, the P − 15 peak of 2-*n*-propylquinoline was found not to be changed in intensity due to the presence of such dimeric products.

Sample A: *m/e* (rel intensity) 346 (5), 343 (5), 341 (3), 340 (7), 326 (4), 325 (8), 202 (8), 201 (26), 200 (84), 175 (8), 174 (29), 173 (100), 172 (32), 171 (71), 159 (8), 158 (24), 157 (0), 156 (0), 145 (16), 144 (47), and 131 (3).

Sample B: *m/e* (rel intensity) 340 (6), 339 (0), 338 (19), 324 (6), 323 (16), 200 (6), 199 (13), 198 (75), 196 (19), 172 (19), 171 (100), 170 (81), 159 (0), 158 (0), 157 (0), 156 (28), 143 (81), 132 (22), and 129 (6).

Thus, it is noteworthy that sample C shows peaks <171 at *m/e* (rel intensity) 170 (35), 158 (13), 157 (13), 156 (11), 145 (11), 144 (41), 143 (24), 131 (2), 130 (2), and 129 (0).

All three samples were then individually subjected to fractional distillation and the MS analyses repeated at 15 eV on the isolated 2-*n*-propylquinolines.

Sample A: *m/e* (rel intensity) 173 (7), 172 (4), 171 (4), 158 (9), 157 (2), 156 (2), 145 (22), 144 (100), 143 (35).

Sample B: *m/e* (rel intensity) 171 (12), 170 (2), 169 (2), 157 (2), 156 (8), 144 (18), 143 (100), 142 (4).

Sample C: *m/e* (rel intensity) 173 (4), 172 (5), 171 (5), 170 (2), 158 (10), 157 (10), 156 (10), 145 (18), 144 (80), 143 (100), 142 (8).

Photochemical Reaction of 2-Allyl-1,2-dihydroquinoline. A 4.2-g sample (25 mmol) in 200 ml of freshly distilled and deoxygenated benzene was irradiated in a photochemical reactor equipped with low-pressure mercury vapor lamps (254 nm) for a period of 24 hr. After removal of the solvent, a NMR analysis showed the presence of 60% quinoline, 20% 2-*n*-propylquinoline, and 20% starting material.

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Registry No.—**3a,** 55570-22-4; **3b,** 55570-23-5; **4a,** 1613-34-9; **4b,** 1613-32-7; **5b,** 55570-24-6; **6b,** 55570-25-7; **7,** 55570-26-8; **10,** 55570-27-9; **11,** 38178-76-6; **16,** 38178-79-9; **17b,** 38178-81-3; **17b** free base, 33538-26-0; **18,** 491-35-0; **21,** 55570-28-0; 2,4-dichloroquinoline, 703-61-7; 4-*n*-propylquinoline, 20668-44-4; 2-methylquinoline, 91-63-4; allyl chloride, 107-05-1; quinoline, 91-22-5; vinyl chloride, 75-01-4; 2-vinylquinoline, 772-03-2; 2-deuterioquinoline, 15793-81-4; 2-(2-deuterioethyl)quinoline, 55570-29-1; phenyllithuim, 591-51-5; 2,4-dideuterioquinoline, 55570-30-4; phenyl chloride, 108-09-7; 4-allyl-2-methylquinoline, 38178-77-7; 4-allyl-2-methyl-1,2-dihydroquinoline, 38178-78-8; *cis*-2-methyl-4-*n*-propyl-1,2,3,4-tetrahydroquinoline, 55570-31-5; *trans*-2-methyl-4-*n*-propyl-1,2,3,4-tetrahydroquinoline, 55570-32-6; *trans*-2-propenylquinoline, 55570-33-7.

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Diquinocyclopropanones, Diquinoethylenes, and the Anion-Radical and Free-Radical Intermediates in Their Formation[1]

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Reaction of trichlorocyclopropenium tetrachloroaluminate with 2 equiv of hindered phenols followed by hydrolysis leads to bis(hydroxyaryl)cyclopropenones (**1**). These are converted upon oxidation to diquinocyclopropanones (**2**), which lose carbon monoxide spontaneously, forming diquinoethylenes (**4**). When photolyzed, compounds **1** lose carbon monoxide, giving bis(hydroxyaryl)acetylenes (**3**), which can be oxidized reversibly to **4**. The free-radical and anion-radical intermediates in the oxidation of **1c** to **2c** and **3c** to **4c** have been studied by electron spin resonance spectroscopy. The hyperfine splitting constants for the anion radicals of **2c**, **4c**, and related quinonoid compounds are rationalized by molecular orbital calculations.

The triquinocyclopropanes (**5**), brilliant blue dye-like compounds, are obtained by reaction of trichlorocyclopropenium tetrachloroaluminate with 2,6-disubstituted phenols followed by deprotonation and oxidation.[2] The reaction of $C_3Cl_3^+$ with aromatic hydrocarbons can also be controlled so that only two of the three chlorine atoms are replaced. The product of this reaction, after hydrolysis, is a diarylcyclopropenone.[3]

This paper reports the reaction of 2,6-dialkylphenols with $C_3Cl_3^+$, leading to bis(hydroxyaryl)cyclopropenones **1a–c**. These compounds undergo oxidation to bright purple diquinocyclopropanones, **2**. The latter can be reduced back to **1** if the reduction is carried out immediately, but if **2a–c** are allowed to stand in solution they spontaneously lose carbon monoxide to give the cumulene derivatives **4a–c**. These are magenta-colored solids (λ_{max} 486 nm), which we term diquinoethylenes.

The stability of diquinoethylenes depends on the alkyl groups: **4c** (R = *tert*-butyl) is stable and unreactive, **4b** (R = isopropyl) is isolable but reacts with water, and **4a** (R =