reaction mixture was stored at 0° for 20 hours and then decanted onto 100 g. of cracked ice containing 35 cc. of 3 *N* hydrochloric acid. The formed precipitate was separated, heated with 150 ml. of water and filtered. The water-insoluble product, 5.2 g. (19%), m.p. 149–153°, was recrystallized (benzene) and melted at 149–151° not depressing the melting point of authentic 2-amino-4-anilino-6-dichloromethyl-*s*-triazine,[23] mixed m.p. 150–152°.

The picrate melted at 206° (ethanol). The mixed melting point with authentic picrate was not depressed, m.p. 205°.

Anal. Calcd. for $C_{16}H_{12}Cl_2N_8O_7$: C, 38.7; H, 2.4. Found: C, 38.7; H, 2.4.

2-Amino-4-anilino-6-(α-hydroxyethyl)-*s*-triazine.—A mixture of 8.9 g. (0.05 mole) of phenylbiguanide, 4.1 g. (0.025 mole) of lactide and 50 ml. of acetonitrile was heated under reflux for 16 hours. When cool, the reaction mixture was decanted into 100 ml. of water. The oil which formed was separated, dissolved in 30 ml. of methanol and added to the filtrate. After standing 24 hours, the formed crystals (6.0 g.) were separated and recrystallized (acetonitrile), yielding 4.5 g. (39%) of product which melted at 142–145°.

Anal. Calcd. for $C_{11}H_{12}N_5O$: C, 57.6; H, 4.8. Found: C, 57.0; H, 5.6.

The picrate melted at 199° (water).

Anal. Calcd. for $C_{17}H_{16}N_8O_8$: C, 44.4; H, 3.5; N, 24.4. Found: C, 44.5; H, 3.7; N, 24.0.

2-Amino-4-anilino-6-(ureidomethyl)-*s*-triazine.—A solution of 7.3 g. (0.05 mole) of ethyl hydantoate in 50 ml. of methanol was treated with 8.9 g. (0.05 mole) of phenylbiguanide and the reaction stored at 20° for 4 days. The reaction mixture was added to 50 ml. of water and crystals (1.65 g.) were separated. Recrystallization (dimethylformamide–ether) yielded 1.44 g. (11%) of product which melted at 227° dec.

Anal. Calcd. for $C_{11}H_{13}N_7O$: C, 51.0; H, 5.1; N, 37.8. Found: C, 51.4; H, 5.0; N, 37.6.

2-Amino-4-anilino-1,3,5-triazin-6-ylacetic acid was obtained from phenylbiguanide and diethyl malonate in 20% yield and melted at 241° dec. (dimethylformamide–methanol).[24]

Anal. Calcd. for $C_{11}H_{11}N_5O_2$: C, 53.9; H, 4.5; N, 28.6. Found: C, 53.9; H, 4.6; N, 28.8.

2-Amino-4-anilino-1,3,5-triazin-6-ylacetonitrile was obtained from phenylbiguanide and ethyl cyanoacetate in 38% yield and melted at 149–152° (water).[25]

Anal. Calcd. for $C_{11}H_{10}N_6$: C, 58.4; H, 4.5; N, 37.1. Found: C, 58.5; H, 4.5; N, 37.2.

Acknowledgment.—The authors are indebted to Dr. G. Ungar and his staff for the pharmacological screening of the compounds.

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[23] S. L. Shapiro and C. G. Overberger, THIS JOURNAL, **76**, 97 (1954), report m.p. 154–155°.

[24] Reference 11 reported m.p. 239–240°.

[25] Reference 11 reported m.p. 152–153°.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE AND ST. LOUIS UNIVERSITY]

The Preparation and Rearrangement of 2-Allyl-1,2-dihydroquinoline

BY HENRY GILMAN, JOHN EISCH[1] AND THEODORE S. SODDY

RECEIVED JANUARY 15, 1959

The interaction of quinoline and allylmagnesium chloride in tetrahydrofuran with subsequent hydrolysis and isolation in a nitrogen atmosphere led to 2-allyl-1,2-dihydroquinoline (I). Compound I is thermally isomerized to 2-*n*-propylquinoline (II) and is transformed into 2-propenylquinoline (III) plus some II by hot nitrobenzene oxidation. The identities of II and III were demonstrated by independent syntheses. Attempts to prepare pure 2-allylquinoline (IV) from 2-bromoquinoline and allylmagnesium bromide led instead to a mixture of 2-allylquinoline (IV) and 2-propenylquinoline (III). The isomerization of IV into III was completed by heating this mixture with solid potassium hydroxide. Infrared data were used extensively in detecting the presence of allyl, propenyl and N-H groups in the products of the foregoing reactions. A reasonable course for the isomerization of I into II is proposed and evaluated in terms of the known properties of related systems.

The observation that allylmagnesium bromide in refluxing ether reacts rather readily with aza-aromatic heterocycles to form allylated products occasioned a study of the relative ease with which bases such as pyridine, quinoline and phenanthridine and others undergo this reaction.[2] Synthesis and structural determination showed the products to be α- or γ-allyl-dihydro derivatives of the respective bases. These partially reduced bases from pyridine and the benzopyridines were quite sensitive to oxidation as evidenced by their rapid discoloration in air. By way of illustration, the product from allylmagnesium bromide and quinoline was a pale yellow oil whose infrared spectrum was in accord with that expected of 2-allyl-1,2-dihydroquinoline. However, the broadening of certain spectral bands indicated partial oxidation of the dihydroquinoline presumably to 2-allylquinoline.

In evaluating the allylating ability of allylmagnesium chloride in tetrahydrofuran, it was therefore curious to note that quinoline gave in 80% yield a product whose infrared spectrum suggested the presence of a propenyl (—CH=CH—, bands at 6.0 and 10.3 μ), and not an allyl group.[3] As the spectrum contained only a weak N-H band, it seemed that extensive air oxidation had occurred during the isolation procedure. Consequently it was felt that the propenyl group was generated upon work-up, and not during the addition reaction or subsequent hydrolysis. In order to minimize the effects of atmospheric oxygen the reaction was repeated and the product isolated under a nitrogen atmosphere. The identity of the principal product as 2-allyl-1,2-dihydroquinoline (I) is strongly supported by its infrared spectrum; exceedingly sharp bands at 2.95 (NH), 6.1, 10.0 and 10.9 μ ($C=CH_2$) are in complete accord with this structure. Conversely, bands indicative of a propenyl group (—CH=CH—) are not present.

By comparison of the yields of 2-allyl-1,2-dihydroquinoline obtained by employing, in turn, (a) allylmagnesium chloride in tetrahydrofuran, (b) allylmagnesium chloride in ether and (c) allylmag-

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[1] Department of Chemistry, St. Louis University, St. Louis, Mo.

[2] H. Gilman, J. Eisch and T. Soddy, THIS JOURNAL, **79**, 1245 (1957).

[3] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 34–56.

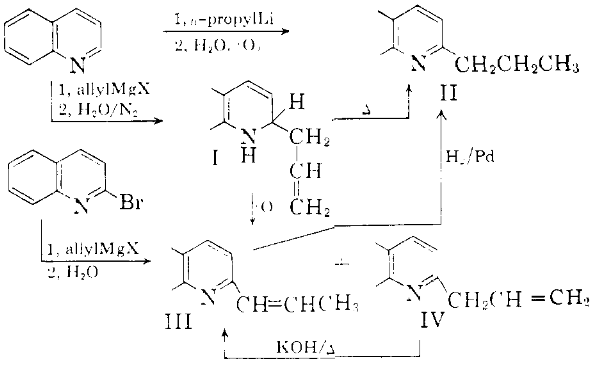
nesium bromide in ether, it was found that method a gave the highest yield of pure product.

The ambiguities arising from the reaction of quinoline and allylmagnesium halides and subsequent work-up in air are due, therefore, to the transformations of I. 2-Allyl-1,2-dihydroquinoline (I), seems to undergo two main reactions of interest here: first, a thermal isomerization to 2-*n*-propylquinoline (II),[4] and, second, oxidation to 2-propenylquinoline (III). Thus compound I was found to isomerize readily to 2-*n*-propylquinoline (II) by heating at 170° under a nitrogen atmosphere. The identity of the product was established by unambiguous synthesis of II from quinoline and *n*-propyllithium. It also has been observed that if the original addition of allylmagnesium halide to quinoline is carried out in refluxing diethyl ether, instead of at room temperature, considerable isomerization to 2-*n*-propylquinoline occurs during the reaction proper (procedure c).

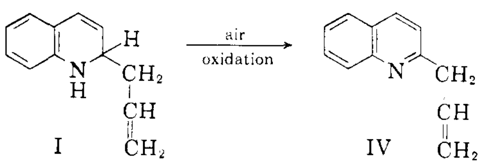
On the other hand, attempted oxidation of 2-allyl-1,2-dihydroquinoline (I) to 2-allylquinoline by nitrobenzene led, instead, to the isomeric 2-propenylquinoline (III), accompanied by some 2-*n*-propylquinoline. The structure of III was verified by catalytic hydrogenation to 2-*n*-propylquinoline and by independent synthesis of III in low yield from quinoline and 1-propenyllithium. 2-Propenylquinoline has strong characteristic bands at 6.0 and 10.3 μ in its infrared spectrum confirming the presence of the —CH═CH—group.[3,4]

Although it appears conceivable that 2-allyl-1,2-dihydroquinoline might give rise to 2-allylquinoline upon mild oxidation, only 2-propenylquinoline eventually could be isolated from such a process as the picrate. As another approach to the elusive 2-allylquinoline (IV), 2-bromoquinoline was treated with allylmagnesium bromide at a low temperature in hopes of obtaining IV by bromine displacement with the allyl group. Subsequent work-up, however, resulted in a 50% yield of a product whose infrared spectrum convincingly indicated the presence of both the allyl (bands at 6.1, 10.0 and 10.9 μ) and the propenyl (6.0 and 10.3 μ) groups. That the product was a mixture of III and IV was satisfactorily shown by heating it with solid potassium hydroxide to complete the isomerization of the allyl to the propenyl side chain, thus giving pure 2-propenylquinoline (III). The infrared spectrum of this distilled product contained sharply defined bands at 6.0 and 10.3 μ, and the bands at 6.1, 10.0 and 10.9 μ had disappeared.

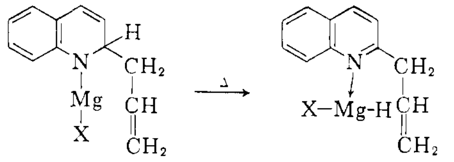
The reactions involved in the preceding preparation and reactions of 2-allyl-1,2-dihydroquinoline (I) are summarized in the equations shown.



The mechanisms of both the isomerization of 2-allyl-1,2-dihydroquinoline (I) to 2-*n*-propylquinoline (II) and the former's oxidation to 2-propenylquinoline involve the rearrangements of unsaturated centers. There is some reason to believe that the two processes may be somewhat interrelated. The fact that the infrared spectrum of the product obtained by heating I under nitrogen to yield 2-*n*-propylquinoline contains perceptible bands at 6.0 and 10.3 μ indicates the presence of some 2-propenylquinoline in the 2-*n*-propylquinoline formed. In addition, whenever 2-allyl-1,2-dihydroquinoline was heated with nitrobenzene to effect dehydrogenation, the product was shown to contain 2-*n*-propylquinoline as well as 2-propenylquinoline. These observations, together with the known behavior of analogous unsaturated systems, lead to a possible pathway for the isomerization and oxidation of I: (a) the formation of 2-allylquinoline (IV) from I,



either by slight air oxidation of the dihydro product[5] or by splitting out of MgXH by the adduct of quinoline and allylmagnesium halide, in the case of isomerization in the refluxing ether reaction mixture.[6]



I (salt) IV (complex with MgXH)

(b) The isomerization (probably base catalyzed) of IV into III, the increase in resonance stabilization with a propenyl side chain being the driving force[7]

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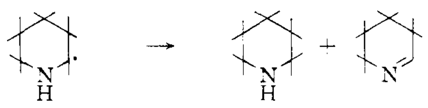
(4) W. Borsche and F. Sell, *Chem. Ber.*, **83**, 78 (1950).

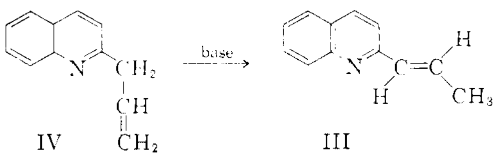
(5) In a recent study of the free-radical additions of amines to olefins W. H. Urry and O. O. Juveland, THIS JOURNAL, **80**, 3322 (1958), found that piperidine interacted with olefins such as ethene and propene to form 2-alkylpiperidines. Finding products indicative of radical-catalyzed addition, they proposed a chain reaction involving formation of a radical on C_2 of piperidine. As their principal chain-breaking step, two such radicals are supposed to disproportionate thus



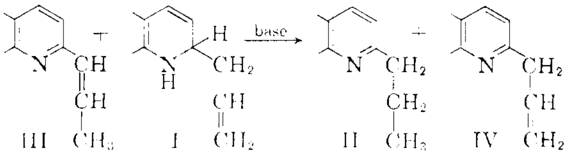
In this case 2-allyl-1,2-dihydroquinoline (I) could form a hydroperoxide due to traces of oxygen and subsequently from radicals suffering the same fate, leading to IV.

(6) The splitting out of metallic hydrides by heating adducts of this type is well substantiated by the work of K. Ziegler and H. Zeiser, *Ber.*, **63**, 1847 (1930), with the adducts of *n*-butyllithium and pyridine bases, and also by the investigations of F. W. Bergstrom and S. H. McAllister, THIS JOURNAL, **52**, 2847 (1930), with Grignard reagents and quinoline at high temperatures.

(7) It should be noted that III may exist as either a *cis* or *trans* isomer; which is formed in these reactions is at present unknown.



(c) The reduction of the 2-propenylquinoline by means of 2-allyl-1,2-dihydroquinoline *via* a hydride ion transfer process (in the case of the reaction mixture isomerization MgXH is probably the active reagent)



In as much as there is considerable chemical analogy between the azomethine linkage and the carbonyl group, compound I may be considered to be similar to a secondary alcohol. Therefore, under basic conditions one might expect the α-hydrogen of I to be transferred to the carbonyl-like system, III. This reaction is therefore the nitrogen system analog of the Meerwein–Ponndorf–Verley reduction.[8] In case of III, however, one is dealing with an α,β-unsaturated azomethine system. Such systems are prone to so-called 1,4-addition to yield the saturated side chain. It is found, for example, that 2-styrylquinoline upon treatment with phenylmagnesium bromide gives after hydrolysis 2-[β,β-diphenylethyl]-quinoline.[9] In like fashion III would form II upon base-catalyzed hydride transfer.[10] The 2-allylquinoline formed in this step would be isomerized subsequently, as in step b, to regenerate III and thus perpetuate the hydride transfer as in step c. The marked ease with which olefinic double bonds adjacent to aromatic systems are reduced by hydride processes is illustrated in the lithium aluminum hydride reduction of cinnamic acid to hydrocinnamyl alcohol.[11]

Therefore, it seems that 2-propenylquinoline may be the actual species facilitating the isomerization of I into II. This would explain why 2-*n*-propylquinoline invariably is formed from the nitrobenzene oxidation of I. Once formed by oxidation, 2-propenylquinoline can compete with the nitrobenzene for the remaining 2-allyl-1,2-dihydroquinoline and thus form 2-*n*-propylquinoline also. Further experimental work will aim at testing these hypotheses. It would be pertinent, for example, to examine whether small amounts of 2-propenylquinoline (III) catalyze the thermal isomerization of 2-allyl-1,2-dihydroquinoline (I) into 2-*n*-propylquinoline (II), as implied in the equation of step c.

Experimental[12]

Starting Materials.—The allylmagnesium halides were prepared in yields ranging from 80 to 90%, either in ether or in tetrahydrofuran solution.[13-15] Except for the slurry obtained with allylmagnesium chloride in ether,[14] the Grignard reagents were analyzed by titrating a hydrolyzed aliquot with standard acid.[16]

The tetrahydrofuran was dried and purified by first shaking with sodium hydroxide pellets, refluxing for several hours over sodium metal and distilling. Final distillation from lithium aluminum hydride was performed immediately before use.

1. **The Reaction of Quinoline with Allylmagnesium Halides. (a) Allylmagnesium Chloride in Tetrahydrofuran.**—To a stirred solution of 12.9 g. (0.1 mole) of pure quinoline in 50 ml. of tetrahydrofuran at room temperature was added dropwise 0.1 mole of allylmagnesium chloride in 130 ml. of tetrahydrofuran over a period of 30 minutes. A clear, reddish-brown solution developed, whose color in reflected light was somewhat green. After a five-hour stirring period the reaction solution was hydrolyzed with 125 ml. of saturated ammonium chloride solution while the flask was cooled in an ice-bath. Under nitrogen the straw-colored ether layer was separated from the aqueous layer and shaken with Drierite. With maintenance of the protective nitrogen atmosphere the solvent was removed by distillation and the residue was fractioned through a 20-cm. Hempel column at 1.5 mm. pressure. The following light yellow-colored fractions, were taken: (1) 84–87°, 2.43 g., n^{25}_D 1.6060; (2) 87–89°, 3.85 g., n^{25}_D 1.6045; (3) 89–90°, 6.35 g., n^{25}_D 1.6032; (4) 90°, 1.0 g., n^{25}_D 1.6025. The infrared spectra were obtained immediately to lessen the chances of air oxidation. The spectra of the fractions were almost identical and contained the bands[3]: 2.95 (N–H), 3.3–3.55 (three bands, alkyl-like group), 6.05 (vinyl, $C{=}CH_2$ grouping), 10.05 and 10.9 ($-CH{=}CH_2$), 14.1 μ (NH rocking). The presence of these bands, together with the absence of bands at 10.3 and 5.95 μ, support the conclusion that the major product is 2-allyl-1,2-dihydroquinoline. The slight decrease in the refractive indices of the fractions is explicable in terms of a small content of 2-*n*-propylquinoline (n^{25}_D 1.5830),[4] resulting from thermal rearrangement of 2-allyl-1,2-dihydroquinoline. The total yield was 13.63 g. or 79.8% of the theoretical.

A check run employing 0.2 mole of each of the reactants gave 26.05 g. or a 76.4% yield. Fractions taken at 2.0 mm. pressure were: (1) 85°, 0.63 g., n^{25}_D 1.6021; (2) 85–87°, 22.27 g., n^{25}_D 1.6002; (3) 87–89°, 3.16 g., n^{25}_D 1.5885. Due to the larger amount of tetrahydrofuran employed in this run the removal of solvent required lengthier heating of the reaction mixture. Consequently, fraction 3 as indicated by its infrared spectrum was largely 2-*n*-propylquinoline with traces of 2-allyl-1,2-dihydroquinoline (weak bands at 3.0, 6.1, 10.0 and 10.9 μ) and probably 2-propenylquinoline (weak bands at 6.0 and 10.3 μ).

The 2-allyl-1,2-dihydroquinoline was difficult to obtain perfectly pure, for redistillation always caused extensive isomerization to 2-*n*-propylquinoline. Moreover, the pale yellow-colored product darkened upon exposure to air. The original odor of 2-allyl-1,2-dihydroquinoline (pleasantly reminiscent of aromatic amines) became a piercing, heavy unpleasant odor upon air oxidation. A hydrogen analysis indicated a partial conversion of the dihydro intermediate to the quinoline structure.

Anal. Calcd. for $C_{12}H_{13}N$: H, 7.60; for $C_{12}H_{11}N$: H, 6.55. Found: H, 7.21.

(b) Allylmagnesium Chloride in Diethyl Ether.—To a stirred solution of 25.8 g. (0.2 mole) of pure quinoline in 100 ml. of dry ether at room temperature was added the white slurry of allylmagnesium chloride in 150 ml. of ether (prepared from 6.66 g. (0.274 g.-at.) of magnesium turnings and 19.2 g. (0.25 mole) of allyl chloride) over a period of 20

Presumably the *trans* isomer would predominate under equilibrating conditions. L. Horwitz, THIS JOURNAL, **77**, 1687 (1955), has reported the preparation of *cis*- and *trans*-2-styrylquinolinium compounds.

(8) W. von E. Doering and T. C. Ashner, *ibid.*, **75**, 393 (1953).

(9) A. Hoffman, M. W. Farlow and R. C. Fuson, *ibid.*, **55**, 2000 (1933).

(10) There is much recent evidence in support of such base-catalyzed reduction processes with nitrogen systems. *Cf.* E. J. Pratt and E. J. Frazza, *ibid.*, **76**, 6174 (1954); M. Avramoff and Y. Sprinzak, *ibid.*, **78**, 4090 (1956).

(11) R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

(12) All melting points are uncorrected. Operations involved in the preparation and reactions of the organometallic reagents were performed in an atmosphere of dry, oxygen-free nitrogen.

(13) H. Gilman and J. H. McGlumphy, *Bull. soc. chim. France*, **43**, 1325 (1928).

(14) M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).

(15) H. Normant, *Compt. rend.*, **239**, 1510 (1954).

(16) H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, THIS JOURNAL, **45**, 150 (1923).

minutes. The reaction mixture became tan in color with the onset of spontaneous reflux. After the suspension had been heated under reflux with stirring for 18 hours, the color had turned a dark purple. Subsequent hydrolysis with 200 ml. of saturated ammonium chloride solution resulted in a red ethereal layer which was worked up under nitrogen. Fractional distillation through a 20-cm. Hempel column at 1.5 mm. gave the fractions: (1) 60–66°, 4.82 g., n^{25}D 1.6200; (2) 70–101°, 3.17 g., n^{25}D 1.6188; (3) 102–105°, 5.41 g., n^{25}D 1.6088; (4) 106–110°, 4.17 g., n^{25}D 1.6059 and a viscous, orange residue of 10.09 g. The infrared spectra of fractions 3 and 4 were very similar to the spectrum of 2-allyl-1,2-dihydroquinoline obtained in method a. However, a definite band at 12.3 μ indicated that fraction 3 contained some quinoline. The crude yield was 8.58 g. (25%) and recovery of quinoline was 31%.

(c) **Allylmagnesium Bromide in Diethyl Ether.**—In a manner similar to that described in parts a and b, 38.8 g. (0.3 mole) of quinoline in 150 ml. of dry ether was treated with 0.45 mole of allylmagnesium bromide in 500 ml. of ether over the course of 60 minutes. The wine-colored solution was heated under reflux for 18 hours (slow gas evolution) and then hydrolyzed. Work-up and distillation under nitrogen yielded these fractions: at 1.2 mm., (1) 68–89°, 1.8 g., n^{25}D 1.6008; (2) 90–98°, 3.4 g., n^{25}D 1.6093; (3) 99–103°, 12.5 g., n^{25}D 1.6041; (4) 103–112°, 23.5 g., n^{25}D 1.5922; at 2.0 mm., (5) 115–120°, 2.9 g., n^{25}D 1.5840; (6) 120–140°, 2.9 g., n^{25}D 1.5749. Total crude yield of allylated quinoline (inclusive of 2-*n*-propylquinoline) was 45.2 g. (88%). Infrared spectral comparisons showed fraction 3 to be contaminated with quinoline (band at 12.3 μ) and fraction 4 to contain a considerable amount of 2-*n*-propylquinoline (band at 12.0 μ). Fractions 5 and 6 were largely 2-*n*-propylquinoline.

It seems fair to state from the results of methods a, b and c, that the milder conditions of utilizing allylmagnesium chloride in tetrahydrofuran at room temperature offers the best method of obtaining the 2-allyl-1,2-dihydroquinoline with a minimum of isomerization to 2-*n*-propylquinoline.

2. **Transformations of 2-Allyl-1,2-dihydroquinoline.** (a) **Thermal Isomerization.**—Any extensive heating in the preparation of 2-allyl-1,2-dihydroquinoline, either in the reaction proper or in removal of the solvent from the reaction extract, led to the formation of considerable quantities of 2-*n*-propylquinoline (compare above). For example, 0.1 mole of quinoline was treated with allylmagnesium chloride in tetrahydrofuran according to procedure a above, and the mixture was worked up without a nitrogen atmosphere. After the tetrahydrofuran was distilled off, the residue was heated at 170° for 12 hours. Distillation of the residue thereupon gave 14 g. (72%) of product, b.p. 87° (1 mm.), n^{25}D 1.5870. The picrate of the compound melted at 159–160°. Comparison of the infrared spectra of the distillate and its picrate with those of authentic 2-*n*-propylquinoline and its picrate indicated that the product of heating the hydrolyzed Grignard adduct was principally 2-*n*-propylquinoline.

Heating a sample of 2-allyl-1,2-dihydroquinoline, n^{25}D 1.6035 (obtained as in procedure a above) under nitrogen at 170° for three hours gave a liquid n^{25}D 1.5985 (undistilled), whose infrared spectrum was almost identical with that of 2-*n*-propylquinoline except for the presence of definite bands at 6.0 and 10.3 μ. These bands are rather good indication that traces of 2-propenylquinoline are present. The allylic bands[3] at 10.05 and 10.9 μ ($-CH=CH_2$) and the NH band at 2.95 μ had disappeared almost completely.

(b) **Nitrobenzene Oxidation.**—Attempts to transform 2-allyl-1,2-dihydroquinoline into 2-allylquinoline by oxidation with nitrobenzene led, in general, to 2-propenylquinoline contaminated with some 2-*n*-propylquinoline. Thus, the residue isolated from a 0.1-mole interaction of quinoline and allylmagnesium chloride as in procedure a was oxidized with nitrobenzene for 30 minutes at 160°. After removal of the nitrobenzene, the residue yielded, upon distillation under pressure, 9.0 g. (52%) of product, n^{20}D 1.6170. A picrate was prepared and after several recrystallizations from ethanol melted at 182–184°, dec. (lit.[4] 183–184°). This proved to be 2-propenylquinoline picrate.

The low value of the refractive index (*cf.* below) and the similarity of most of the infrared spectrum to that of 2-*n*-propylquinoline indicated that the oxidation is not clear-cut. Principal spectral bands[2] were at 6.1 and 10.3 μ ($-CH=CH-$).

3. **Structure Proof of the Products.** (a) **2-*n*-Propylquinoline** was synthesized by the interaction of *n*-propyllithium and quinoline according to a published procedure.[2] Oxidation of the dihydro adduct and distillation gave a light green oil, n^{20}D 1.5865, b.p. 85° (1.5 mm.). The picrate formed yellow needles, m.p. 162–163°. The infrared spectrum showed a moderate band at 3.0 μ (some imino tautomer ?, NH–) and strong bands[3] at 3.4, 10.4, 12.0 and 12.7 μ.

(b) **The Catalytic Hydrogenation of 2-Propenylquinoline.**—To a solution of 5.0 g. (0.029 mole) of 2-propenylquinoline (from nitrobenzene oxidation of 2-allyl-1,2-dihydroquinoline) in 75 ml. of absolute ethanol was added 1 g. of palladium-on-calcium carbonate catalyst. The mixture was treated with hydrogen under 45 lb./sq. in. on a rocking hydrogenation apparatus at 20°. After 18 hours (pressure dropped to 42.5 lb./sq. in.) the catalyst was filtered off, the ethanol was removed and the residue was distilled to give 2.5 g. (50%) of a pale green oil, n^{20}D 1.5850, picrate, m.p. 162–163° (lit.[4] 164°). Both infrared spectral comparisons of compound and mixture melting determination of its picrate with authentic samples confirmed the product to be 2-*n*-propylquinoline.

(c) **2-Propenylquinoline.**—As nitrobenzene oxidation of 2-allyl-1,2-dihydroquinoline did not yield pure 2-propenylquinoline, it was decided to prepare this compound in another fashion. First, the interaction of quinoline and propenyllithium,[17] followed by the nitrobenzene oxidation of the hydrolyzed product, was carried out in the usual fashion. However, work-up gave only 18% of product, b.p. 80° (0.01 mm.), picrate, m.p. 183–184°. The infrared spectrum of the picrate was superimposable upon that of 2-propenylquinoline picrate from II, b above.

Another method of obtaining 2-propenylquinoline is the interaction of 2-bromoquinoline and allylmagnesium bromide in ether. The intention had been to prepare pure 2-allylquinoline. However, isomerization occurred in the course of reaction. Thus to 0.092 mole of allylmagnesium bromide in 95 ml. of ether was added dropwise a solution of 17.9 g. (0.086 mole) of 2-bromoquinoline dissolved in 55 ml. of ether. During the 25-minute addition period the stirred contents were cooled in an ice-bath. After an initial blue fluorescence a deep carmine solution developed. The reaction mixture was hydrolyzed with 125 ml. of saturated ammonium chloride solution after 4 hours stirring at 0 to 15°. Separation of the red ether layer, storing over Drierite and final removal of solvent gave a residue which was fractionated at 10 mm. through a 20-cm. Hempel column: (1) 129–133°, 3.9 g., n^{26}D 1.6271; (2) 133–134°, 3.4 g., n^{26}D 1.6260. The infrared spectra of fractions 1 and 2 were almost identical. The presence of equally strong bands at 6.0 and 6.1 μ, at 10.0 and 10.9 μ, and at 10.3 and 10.6 μ showed clearly the reaction product obtained in 50% yield contained both 2-allylquinoline (6.1, 10.0 and 10.9 μ) and 2-propenylquinoline (6.0 and 10.3 and 10.6 μ).

Proof that this was the case was obtained by heating the product at 150° with potassium hydroxide pellets to complete the isomerization to 2-propenylquinoline. The main fraction obtained upon subsequent distillation had a boiling point of 90° (1.8 mm.), n^{25}D 1.6359. The infrared spectrum showed no traces of bands at 6.1, 10.0 and 10.9 μ. Exceedingly sharply defined bands occurred at 6.0, 8.8, 9.1, 10.3, 10.6 and 11.6 μ. A picrate of densely matted needles melted at 182.5–184° dec. Both mixture melting point and examination of its spectrum proved it to be authentic 2-propenylquinoline picrate.[4]

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[17] E. A. Braude, J. A. Coles and C. J. Timmons, *Nature*, **166**, 58 (1950).