followed spectrophotometrically by the change of optical density at 300 mμ. Chimyl alcohol was used as a standard, as follows. A solution of 1.84 mg. of chimyl alcohol in 4 ml. of 95% ethanol was treated with 0.1 ml. of a 0.2 *M* phosphate buffer solution (pH 7.4), and to this mixture was added 1.0 ml. of a 0.01 *M* sodium periodate solution. The change of optical density with time was recorded; the optical density at the start of the reaction was obtained by extrapolation.[19] One molar equivalent of periodate was consumed in 5 hr, which was taken as the standard time required for complete reaction under these conditions. In separate duplicated runs, the *n*-dodecyl glycerol ethers obtained respectively from components A and B each contained 0.47 ± 0.03 mole of 1,2-glycol/mole of substance.

(19) G. V. Marinetti and G. Rouser, *J. Am. Chem. Soc.*, **77**, 5345 (1955).

Reaction of Pyridine and Quinoline N-Oxides with Phenylmagnesium Bromide

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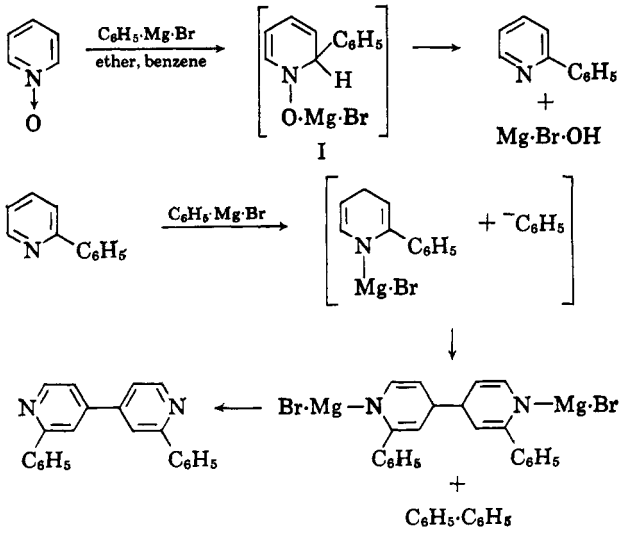
Reactions of pyridine and quinoline N-oxides with phenylmagnesium bromide in tetrahydrofuran are described. Pyridine N-oxide is converted to 1-hydroxy-2-phenyl-1,2-dihydropyridine (III) in 60–80% yield. III is easily dehydrated to give 2-phenylpyridine. Quinoline N-oxides (X) are converted to 2-phenylquinoline N-oxide derivatives (XI) as main products with 2-phenylquinolines (XII) as by-products. If the reaction is carried out at lower temperature 1-hydroxy-2-phenyl-1,2-dihydroquinoline (VII) is obtained.

There is considerable literature dealing with the Grignard reaction of pyridine and quinoline compounds,[1-9] but only a few references are available concerning the Grignard reaction with their N-oxides. In 1936, Colonna[10] reported the reaction of pyridine N-oxide and quinoline N-oxide with phenylmagnesium bromide in ether to give 2-phenylpyridine and 2-phenylquinoline, respectively. Ochiai[11] re-examined this reaction in benzene as a solvent, and described the reaction as shown in Scheme I with 2-phenylpyridine (13%), 2,2′-diphenyl-4,4′-bipyridine (4%) and biphenyl as the products. However, neither of the dihydro derivatives (I or II) was isolated as stable intermediates.

During the course of an investigation on the synthesis and reactions of phenylpyridine derivatives, attention in our laboratory was focused upon the Grignard reaction mentioned above. Because of poor yields, the Grignard reaction has not been a practical method of synthesis. Therefore, it was thought advisable to find improved conditions or another route of synthesis for 2-phenylpyridine. On the other hand, tetrahydrofuran (THF) is known to an excellent solvent for the Grignard reaction.[12] This paper describes the reaction of pyridine and quinoline N-oxides with phenylmagnesium bromide in THF as a solvent in place of ether or benzene to give dihydro intermediates as stable compounds in good yields. This method is practical for the synthesis of 2-phenylpyridine and 2-phenylquinoline derivatives.

SCHEME I[11]

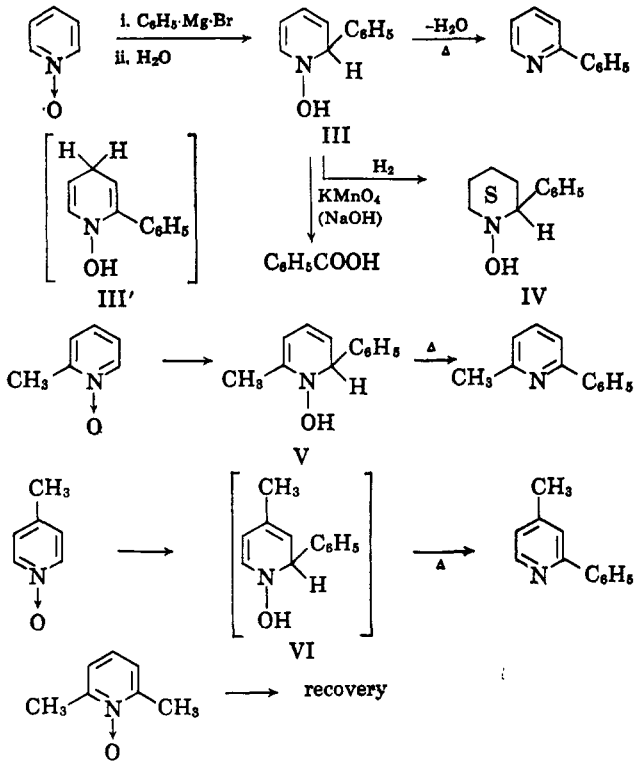


Reaction of Pyridine N-Oxide with Phenylmagnesium Bromide.—When pyridine 1-oxide was allowed to react with phenylmagnesium bromide in THF, white needles of a compound, $C_{11}H_{11}ON$ (III), were obtained as the main product (60–80%) with 2-phenylpyridine and 2,2′-diphenyl-4,4′-bipyridine as by-products. Compound III was soluble in 10% sodium hydroxide and in organic solvents except for petroleum ether, but it was insoluble in 10% sodium carbonate and 10% hydrochloric acid. The ferric chloride color test for phenolic compounds was negative. A dry distillation with zinc dust or heating of III to 200° gave 2-phenylpyridine and water. Upon treatment with acetic anhydride, III was converted to 2-phenylpyridine. The oxidation of III with potassium permanganate in sodium hydroxide solution gave benzoic acid (see Scheme II).

The n.m.r. spectrum of III shows a doublet at τ 1.5 (J = 10 c.p.s., one proton at the 2-position of the pyridine ring), a complex multiplet at 2.51–2.73 (five protons of benzene), a complex multiplet at 2.98–4.05 (four vinyl protons of the pyridine ring), and one proton at 0.8 (=N—OH). The presence of methylene protons was not observed. These data are consistent with the 1,2-dihydropyridine structure III, but not with the isomeric 1,4-dihydro compound III′.

(1) F. Bergstrom and S. McAllister, *J. Am. Chem. Soc.*, **52**, 2849 (1930).
(2) H. Gilman and J. Eish, *ibid.*, **79**, 1245 (1957).
(3) W. Rosenthal and E. Bergman, *J. prakt. Chem.*, [2] **135**, 267 (1932).
(4) W. Veer and S. Goldschmidt, *Rec. trav. chim.*, **65**, 793 (1943).
(5) A. Jong, H. Hertog, and J. Wibaut, *ibid.*, **70**, 989 (1951).
(6) K. Thomas and D. Jerchel, *Angew. Chem.*, **70**, 719 (1958).
(7) C. Hauser and M. Weiss, *J. Org. Chem.*, **14**, 310 (1949).
(8) N. Goetz-Luthyl, *J. Am. Chem. Soc.*, **71**, 2254 (1949).
(9) R. Benkeser and D. Holton, *ibid.*, **73**, 5861 (1951).
(10) M. Colonna, *Chem. Abstr.*, **30**, 3420 (1936).
(11) E. Ochiai and K. Arima, *Yakugaku Zasshi*, **69**, 51 (1949).
(12) H. Normant in "Advances in Organic Chemistry" Vol. II, R. Raphael, E. Taylor, and H. Wynberg, Ed., Interscience Publishers Inc., N. Y., p. 1.

SCHEME II



Upon catalytic reduction of III with palladium–Norit in methanol, 1-hydroxy-2-phenylpiperidine (IV) was obtained.

Attempts to prepare 2-phenylpyridine 1-oxide by oxidation of III failed; for example, refluxing with nitrobenzene in ethanol resulted in the recovery of the starting material (III), and use of potassium ferricyanide or chloroanil as oxidizing agents resulted in the formation of resin.

Mostly starting material was obtained from the attempted reaction of 2,6-lutidine 1-oxide with phenylmagnesium bromide,[13] but 2-picoline 1-oxide reacted similarly as in the case of pyridine 1-oxide to give 1-hydroxy-2-phenyl-6-methyl-1,2-dihydropyridine (V) in a yield of 55% with small amounts of 2-phenyl-6-methylpyridine, biphenyl, and phenol as by-products.

Compound V was heated on a water bath with acetic anhydride, as in the case of 2-phenylpyridine derivative (III), to give 2-phenyl-6-methylpyridine in a good yield. It was also obtainable by heating V on an oil bath to 180°.

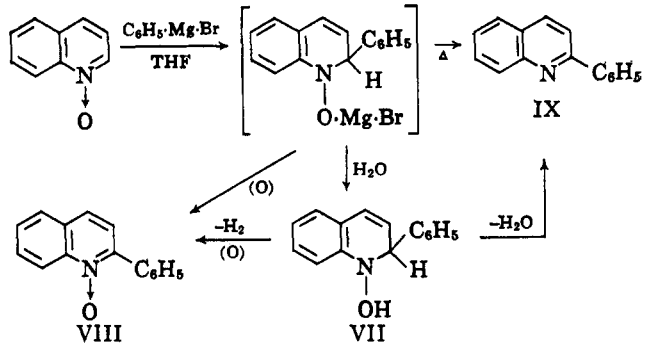
4-Picoline 1-oxide was converted into the dihydro derivative (VI), which was not isolated as a crystalline solid, and the heating of VI with acetic anhydride gave 2-phenyl-4-methylpyridine.

Reaction of Quinoline N-Oxide with Phenylmagnesium Bromide.—It was of interest to see whether the reaction of quinoline 1-oxide with phenylmagnesium bromide was similar to that with pyridine 1-oxide. Colonna and Risalti[14] reported the reaction of quinoline 1-oxide with phenylmagnesium bromide in ether to give 2-phenylquinoline in a yield of 30%. We re-examined this reaction in THF under reflux and have found that 2-phenylquinoline 1-oxide was the main

(13) In this reaction a low yield of 1-oxido-2-methyl-6-pyridylmethylmagnesium bromide was observed, and the details of its reaction is now under investigation.

(14) M. Colonna and A. Risalti, *Gazz. chim. ital.*, **83**, 58 (1953).

SCHEME III



product (60%) with 2-phenylquinoline as a by-product (30%) (expt. 2 in Table 1). Careful treatment at room temperature (15–20°) gave 1-hydroxy-2-phenyl-1,2-dihydroquinoline (VII) in 40% yield (expt. 1 in Table I). Table I shows the summary of this reaction.

TABLE I

REACTION OF QUINOLINE 1-OXIDE WITH PHENYLMAGNESIUM BROMIDE IN TETRAHYDROFURAN

Expt.	Quinoline 1-oxide mole	C_6H_5MgBr, moles	Temp., °C.	Reaction time, hr.	Product, % VII	VIII	IX
1	1	2	10–15[a]	7	40	30	17
2	1	2	Reflux	5	0	60	30
3	1	1	Reflux	5	0	20	45
4	1	5	Reflux	4	0	0	95

[a] At room temperature.

The dihydro derivative (VII) was dissolved in acetic anhydride and was allowed to stand to be converted into 2-phenylquinoline (IX) (see Scheme III) in a good yield. Compound VII is not so stable as 1-hydroxy-2-phenyl-1,2-dihydropyridine (III) and was transformed into 2-phenylquinoline (IX) by dehydration, even under a mild condition such as refluxing in THF. The most significant difference between III and VII is that VII was easily oxidized to give 2-phenylquinoline 1-oxide (VIII) when VII was bubbled in THF or allowed to stand for several days at room temperature. When this reaction was run at a higher temperature, for example, in boiling THF, the dehydration reaction was predominant over oxidation reaction resulting in the formation of 2-phenylquinoline (IX). Compound VIII was easily reduced to 2-phenylquinoline (IX) by catalytic reduction with Raney nickel.

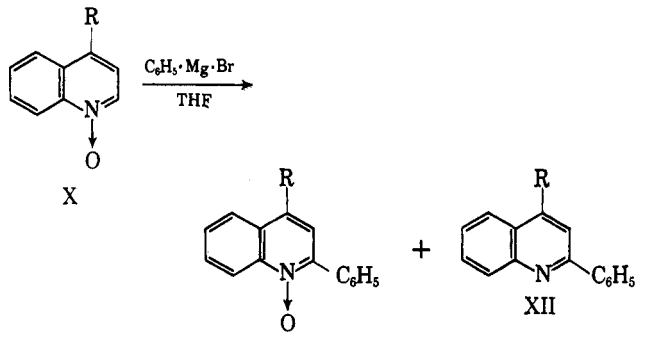
In regard to the reaction of phenylmagnesium bromide with pyridine and quinoline N-oxides, Hayashi, *et al.*,[15,16] have reported on the reaction of benzodiazines such as quinazoline or quinoxaline N-oxide with phenylmagnesium bromide in ether to give 2-phenylbenzodiazine N-oxide. They thought this reaction was a special case observed only with benzodiazine N-oxide. However, our work shows that it is not an exceptional reaction.

Attempts were made to treat phenylmagnesium bromide with 4-substituted quinoline N-oxides (X) such as 4-methoxy (Xa), 4-ethoxy (Xb), 4-chloro (Xc) and 4-methyl (Xd) derivatives as shown in Scheme IV. Although none of 1,2-dihydro-type intermediate was isolated in these experiments, the first step of this re-

(15) E. Hayashi and C. Iijima, *Yakaguku Zasshi*, **82**, 1093 (1962).

(16) E. Hayashi and T. Higashino, *Chem. Pharm. Bull.*, **12**, 434 (1964).

SCHEME IV



a, R = OCH_3
b, R = OC_2H_5
c, R = Cl
d, R = CH_3

action is sure to be the formation of 2-phenyl-1,2-dihydro derivative, and there are two kinds of reactions in the next step. The first one is to form the corresponding 2-phenyl derivative (XII), which is accompanied by dehydration reaction. The other is to form the corresponding N-oxide derivative (XI), which is accompanied by oxidation reaction. Table II summarizes this reaction and shows that the N-oxide derivatives (XI) were always main products.

TABLE II

REACTION OF 4-SUBSTITUTED QUINOLINE N-OXIDE WITH PHENYLMAGNESIUM BROMIDE IN TETRAHYDROFURAN

4-Substituted quinoline 1-oxide (X), mole	C_6H_5MgBr, mole	Temp., °C.	Reaction time, hr.	XI, %	XII, %
a, 1	2	70	7	64	13
b, 1	2	70	7	65	16
c, 1	2	R.T.[a]	24	63	low
d, 1	2	70	6	45	30

[a] At room temperature.

Although the details of the mechanism of the formation of dihydro-type compounds (III, V, and VII) or 2-phenyl N-oxide derivatives is obscure at present, these methods will be useful for synthesizing of 2-phenylpyridine or quinoline derivatives.

Experimental

Preparation of Phenylmagnesium Bromide.—A crystal of iodine was added to 2.4 g. (0.1 g.-atom) of magnesium turnings in dry THF. Bromobenzene (5 g.) was added to the solution at room temperature until the reaction became rapid. Stirring was then started and 10.7 g. (total, 15.7 g., 0.1 mole) of bromobenzene was run in slowly at a rate to cause gentle refluxing. When the addition was complete, the reaction mixture was heated on a steam bath for 1 hr. with stirring and then cooled in an ice bath.

Reaction of Pyridine 1-Oxide with Phenylmagnesium Bromide.—Pyridine 1-oxide (5.5 g., 0.058 mole) in 30 ml. of THF was added dropwise to 0.1 mole of phenyl Grignard reagent and, after stirring for 30 min. at 40°, the reaction mixture was allowed to stand overnight. Water was added and a white pasty precipitate formed. The solvent layer was decanted and the pasty solid was washed with chloroform. The combined solution was condensed *in vacuo* to a dark residue. Crystallization from a small amount of benzene was induced by scratching with a glass rod to give a crystalline solid which, after filtering with suction, had m.p. 128–130°, 7.1 g. Recrystallization from benzene gave white needles of III: m.p. 132°; 5.5 g.; ultraviolet, λ_{max}^{EtOH} 237 mμ (log ε 4.03) and 313 mμ (log ε 4.71).

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09 Found: C, 76.15; H, 6.37; N, 8.12.

Ether was added to the filtrate and extraction with 10% sodium hydroxide and then 10% hydrochloric acid was done. From the sodium hydroxide soluble fraction, .1 g. of material, m.p. 125–129°, was obtained. Recrystallization from benzene gave 0.6 g. of III. Total yield of III was 6.1 g. (67%). The hydrochloric acid extract was made alkaline with potassium carbonate, extracted with ether, dried, and distilled to give 0.5 g. of 2-phenylpyridine (picrate, lit.[8] m.p. 173–175°) and 0.8 g. of 2,2′-diphenyl-4,4′-bipyridine (lit.[11] m.p. 170–173°). The neutral fraction was distilled *in vacuo* to give 0.75 g. of biphenyl.

Reactions of 1-Hydroxy-2-phenyl-1,2-dihydropyridine (III).

1. **Dry Distillation with Zinc Dust.**—One gram of III was distilled with 10 g. of zinc dust *in vacuo* at 200°, then at 240–260° in an oil bath, to give an orange-yellow oil. This was dissolved in 20 ml. of ether and extracted with 10% hydrochloric acid. From the hydrochloric acid soluble fraction 0.32 g. of 2-phenylpyridine was obtained.

2. **Reaction with Acetic Anhydride.**—A solution of 0.7 g. of III in 7 ml. of acetic anhydride was heated for 3 hr. under reflux. After removal of acetic anhydride *in vacuo*, the residue was made alkaline with 10% sodium hydroxide to give an oil, which was extracted with benzene. The benzene solution was purified by alumina chromatography to give 0.4 g. of 2-phenylpyridine.

3. **Oxidation Reaction with Potassium Permanganate.**—Five grams of potassium permanganate in 40 ml. of water was added to a solution of 0.87 g. of III in 10% sodium hydroxide on a steam bath. After the addition had been completed, the coloration of the mixture disappeared, and the solution was heated for another hour. The reaction mixture was filtered; the filtrate was acidified with concentrated hydrochloric acid and extracted with ether. From the ether extract 0.29 g. of benzoic acid was obtained.

4. **Reduction of III.**—A sample of III (0.86 g.) in 20 ml. of methanol was hydrogenated over palladium–Norit (prepared from 5 ml. of 2% palladium chloride and 1.5 g. of Norit) with hydrogen at atmospheric pressure and room temperature. The theoretical amount of hydrogen (224 ml., 2 molar equiv.) was absorbed in about 5 min. After removal of the catalyst by filtration, the filtrate was concentrated *in vacuo*. The residue was dissolved in ether and washed with 10% sodium hydroxide and then with 10% hydrochloric acid. The ether layer was dried over sodium sulfate, evaporated, and distilled *in vacuo* to give 0.4 g. of a colorless oil, b.p. 140° (3 mm.), which solidified upon cooling. Crystallization from petroleum ether gave 0.2 g. of IV as colorless prisms: m.p. 57–58°; ultraviolet, λ_{max}^{EtOH} 260 mμ (log ε 2.30).

Anal. Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.88; H, 8.54; N, 7.57.

Reaction of 2-Picoline 1-Oxide with Phenylmagnesium Bromide.—Following the procedure given for pyridine 1-oxide, the reaction of 2-picoline 1-oxide (2.7 g., 0.026 mole) with 0.03 mole of phenylmagnesium bromide in 40 ml. of THF gave 0.1 g. of phenol as an acidic substance, 0.5 g. of a basic oil, b.p. 120° (10 mm.), and a neutral semisolid. The basic oil was identified as 2-phenyl-6-methylpyridine by admixture with an authentic sample[17] both as picrate derivatives. The neutral semisolid was dissolved in chloroform and purified by use of alumina chromatography to give 0.1 g. of biphenyl and 2.5 g. (54%) of 1-hydroxy-2-phenyl-6-methyl-1,2-dihydropyridine (V): m.p. 101° (white needles from 50% methanol); ultraviolet, λ_{max}^{EtOH} 238 mμ (log ε 4.02) and 314 mμ (log ε 4.70). The infrared absorbtion spectrum of V was quite similar in every respect to that of III.

Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.99; H, 7.06; N, 7.42.

A solution of V (0.56 g.) in 5 ml. of acetic anhydride was treated similarly as described above to give 0.4 g. of a colorless oil whose picrate was identical with 2-phenyl-6-methylpyridine picrate.

Reaction of 4-Picoline 1-Oxide with Phenylmagnesium Bromide.—Employing the same procedure as described above, the reaction of 4-picoline 1-oxide (4.36 g., 0.04 mole) with 0.05 mole of phenylmagnesium bromide in 60 ml. of THF afforded 0.1 g. of phenol as an acidic substance and 0.2 g. of 2-phenyl-4-picoline as a basic oil, picrate m.p. 186–187°, undepressed with an

(17) M. Scholtz, *Ber.*, **28**, 1726 (1895).

authentic sample.[18] The neutral substance was distilled to give 0.3 g. of biphenyl and 1.65 g. of a colorless oil, b.p. 145–150° (10 mm.). This oil was dissolved in ether and extracted with 10% hydrochloric acid. From the hydrochloric acid soluble fraction 1.5 g. of 2-phenyl-4-picoline was obtained. Total yield was 1.7 g. (23%).

Reaction of Quinoline 1-Oxide with Phenylmagnesium Bromide. First Run (under Reflux).—Phenylmagnesium bromide (0.05 mole) in 20 ml. of THF was added to quinoline 1-oxide (3.6 g., 0.025 mole) in 20 ml. of THF with cooling over period of 30 min. The reaction mixture was heated under reflux with stirring for 4 hr. Water was added and the supernatant was decanted. The pasty residue was extracted with chloroform. The combined organic layer was dried and evaporated to give a semisolid. This was washed with ether. The residue, which was insoluble in ether, was crystallized from benzene–petroleum ether (b.p. 60–80°) to give 2-phenylquinoline 1-oxide (VIII), m.p. 144–145°,[19] 3.3 g. (60%).

The ether-soluble layer was condensed and distilled to give 1.5 g. (30%) of 2-phenylquinoline (IX), b.p. 190–200° (8 mm.), m.p. 80–82°, picrate m.p. 192°.[20]

Second Run (at Room Temperature).—Phenyl Grignard reagent (0.04 mole) was added to 2.9 g. (0.02 mole) of quinoline 1-oxide in THF. The reaction mixture was stirred for 7 hr. at room temperature (15–20°) and allowed to stand overnight. In a similar manner to that described above for the reaction of pyridine 1-oxide, the resulting residue was treated with 10% hydrochloric acid and 10% sodium hydroxide. Phenol (0.1 g.) was obtained as an acidic compound. From the hydrochloric acid soluble fraction, 0.8 g. (20%) of 2-phenylquinoline (IX) and 1.7 g. (40%) of 2-phenylquinoline 1-oxide (VIII) were obtained. The neutral fraction was condensed, cooled in an ice bath, and scratched with a glass rod to give a crystalline solid. Recrystallization from dilute methanol gave 1.1 g. (25%) of 1-hydroxy-2-phenyl-1,2-dihydroquinoline (VII) as white needles, m.p. 111°.

Anal. Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.74; H, 6.00; N, 6.24.

Third Run (with Excess Grignard Reagent under Reflux).—Following the procedure given for the first run, the reaction of quinoline 1-oxide (2.9 g.) with 0.1 mole of phenyl Grignard reagent gave 3.8 g. (90%) of 2-phenylquinoline.

Reaction of 1-Hydroxy-2-phenyl-1,2-dihydroquinoline (VII). 1. Thermal Decomposition under Reduced Pressure.—Compound VII (0.2 g.) was placed in a 5-ml. distilling flask and heated on an oil bath to 130° *in vacuo* to give 2-phenylquinoline as a colorless oil, picrate m.p. 192°.

2. Reaction with Acetic Anhydride.—A solution of VII (0.2 g.) in 5 ml. of acetic anhydride was allowed to stand at room temperature overnight. After removal of acetic anhydride by distillation under reduced pressure, the reaction mixture was made alkaline with 10% sodium hydroxide to yield a brown oil. This was extracted with ether. The ether solution was purified by alumina chromatography to give 2-phenylquinoline.

3. Air Oxidation.—Air was bubbled into a solution of VII (0.2 g.) in 10 ml. of THF at room temperature for 3 hr. After being allowed to stand overnight, the solution was evaporated *in vacuo* to give a crystalline solid. Crystallization from benzene–petroleum ether gave 0.07 g. of 2-phenylquinoline 1-oxide, m.p. 144–145°.

Reaction of 4-Methoxyquinoline 1-Oxide (Xa) with Phenylmagnesium Bromide.—Phenylmagnesium bromide (0.01 mole) in 20 ml. of THF was added to 4-methoxyquinoline 1-oxide (0.88 g., 0.005 mole) in 20 ml. of THF, and the reaction mixture was warmed at 50° for 7 hr. with stirring. In a similar manner to that described above for the first run, the resulting residue was treated to give 0.15 g. (13%) of 4-methoxy-2-phenylquinoline (XIIa), lit.[21] m.p. 67°, and 0.8 g. (64%) of 4-methoxy-2-phenylquinoline 1-oxide (XIa), m.p. 119–121°, hydrochloride m.p. 155–156° dec. No depression in melting point was observed on admixture with a sample prepared by the reaction of XIc with sodium methoxide in absolute methanol.

Anal. Calcd. for $C_{16}H_{13}NO_2$: N, 5.57. Found: N, 5.48.

Reaction of 4-Ethoxyquinoline 1-Oxide (Xb) with Phenylmagnesium Bromide.—Following the procedure given for 4-methoxy derivative Xa, the reaction of 4-ethoxyquinoline 1-oxide (Xb, 0.95 g., 0.005 mole) with phenyl Grignard reagent (0.01 mole) gave 0.2 g. (16%) of 2-phenyl-4-ethoxyquinoline (XIIb, colorless needles, m.p. 100–102°, hydrochloride m.p. 196° dec., lit.[21] for picrate m.p. 207–208°) and 0.85 g. (65%) of 2-phenyl-4-ethoxyquinoline 1-oxide (XIb, colorless prisms from benzene–petroleum ether, m.p. 158°).

Anal. Calcd. for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.79; H, 5.76; N, 5.28.

A sample of XIb (0.6 g.) was hydrogenated in 20 ml. of methanol over Raney nickel with hydrogen at atmospheric pressure to give XIIb in almost quantitative yield (0.5 g.).

Reaction of 4-Chloroquinoline 1-Oxide (Xc) with Phenylmagnesium Bromide.—Following the procedure given for the second run (at room temperature), 4-chloroquinoline 1-oxide (Xc, 0.9 g., 0.005 mole) reacted with phenyl Grignard reagent (0.01 mole) to give 0.1 g. of an oily substance (XIIc) and *ca.* 1 g. of white crystals (XIc). The identity of this oil with XIIc was established by the reaction with sodium ethoxide in absolute ethanol to give 4-ethoxy derivative (XIIb). The crystalline solid (XIc) was recrystallized from benzene–petroleum ether to give white needles of XIc, m.p. 122–133°, 0.8 g. (63%).

Anal. Calcd. for $C_{15}H_{10}ClNO$: C, 70.45; H, 3.94; N, 5.49. Found: C, 70.19; H, 4.05; N, 5.39.

Compound XIc (0.6 g.) was treated with sodium ethoxide (prepared from 0.1 g. of sodium and 10 ml. of ethanol) to give 0.5 g. of 4-ethoxy derivative (XIb). 4-Methoxy derivative (XIa) was also obtained by the same reaction of XIc with sodium methoxide.

Reaction of 4-Methylquinoline 1-Oxide (Xd) with Phenylmagnesium Bromide.—Following the procedure given for the first run, 4-methylquinoline 1-oxide (Xd, 0.8 g., 0.005 mole) was treated with phenyl Grignard reagent (0.01 mole) to give 0.33 g. (30%) of 2-phenyllepidine (XIId, lit.[22] m.p. 64–65°) and 0.53 g. (45%) of 2-phenyllepidine 1-oxide (XId, white needles from ether–benzene, m.p. 121°).

Anal. Calcd. for $C_{16}H_{13}NO$: N, 5.95. Found: N, 6.03.

Reduction of XId with Raney nickel afforded XIId in a good yield.

Acknowledgment.—The authors are grateful to Miss Nako Yasuda and Miss Shoko Oizumi for the spectral data and Miss Etsuko Sugawara and Miss Nobuko Nanjo for the elemental analyses.

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(19) M. Colonna and A. Risalti, *Bull. sci. faolta chim. ind. Bologna*, **9**, 82 (1951); *Chem. Abstr.*, **46**, 7102 (1952).

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(22) H. John and F. Noziczka, *J. prakt. Chem.*, [2] **111**, 68 (1925).