half-life of the tracer, the fact that the activity ratios after a contact time of ten minutes or 36 hr. were sensibly the same indicates that equilibrium 2 is at most a very unimportant side

$$(C_2H_5)_2Mg + MgBr_2 \rightleftarrows 2C_2H_5MgBr \qquad (2)$$

reaction with respect to the over-all picture. The results are compatible with an equilibrium of the type

$$(C_2H_5)_2Mg + MgBr_2 \rightleftarrows (C_2H_5)_2Mg{\cdot}MgBr_2 \quad (3)$$

Along the same lines it is interesting to note that the diethylcadmium–cadmium bromide system in tetrahydrofuran shows no exchange under similar conditions.[6]

A more comprehensive investigation of Grignard systems is being contemplated, employing stable isotopes as tracers.

Experimental

Diethylmagnesium.—The diethylmagnesium in ether was prepared by the action of dioxane on an ether solution of ethylmagnesium bromide,[7] followed by removal of the solvents and dissolution in ether.

Labeled Magnesium Bromide.—Mg^{28} was prepared by a spallation reaction involving proton irradiation of a one cc. single crystal of potassium chloride[8] for 1 hr. at a radius equivalent to 350 Mev. in the Synchrocyclotron of the Carnegie Institute of Technology. The crystal was permitted to stand for 2 hr. after it was dismounted from the probe to allow any short-lived material to decay, and it was then dissolved in 50 ml. of water, along with 100 mg. of $Al(NO_3)_3$ and 500 mg. of $MgBr_2$ to serve as carriers. The solution was heated to the boiling point and adjusted to *p*H 8 with ammonium hydroxide in order to precipitate aluminum hydroxide, which was filtered off. The filtrate was diluted to 125 ml. and heated to 60° and 35 ml. of 6 *N* ammonium hydroxide added. Then 30 ml. of 5% 8-hydroxyquinoline in 2 *N* acetic acid was added slowly. The suspension was brought to the boiling point and then permitted to settle for a few minutes. The oxinate of magnesium was collected by filtration and dried.

The greenish-yellow oxinate was mixed intimately with an equal volume of oxalic acid and placed in a fused silica crucible. Careful ignition with a blast burner yielded magnesium oxide as a fine white powder. The magnesium oxide was dissolved in concentrated hydrochloric acid and any excess acid destroyed by adding a few shavings of magnesium metal.

The solution of magnesium chloride was transferred to a graphite crucible enclosed in a Vycor capsule along with 10 g. of Dow atomized magnesium pellets. The capsule was then attached to a vacuum line and carefully pumped out. The capsule was then heated to 800° and kept at that temperature for 1 hr. in order to cause exchange between the Mg and Mg^*Cl_2. The contents of the crucible were permitted to cool, and the capsule was forced open. Under the conditions employed the Mg was obtained as a clean crystalline plug, which had distilled or sublimed from the hot furnace area of the crucible to cooler portions. This plug was crushed and added to 100 ml. of Mallinckrodt Anhydrous Ether in a three-necked flask equipped with a stirrer, addition funnel and Dry Ice–acetone condenser. Bromine was added slowly to the suspension until a considerable quantity of the magnesium had been utilized. Magnesium bromide and ether, in these concentrations, form a two-phase system.[9] The darker lower layer which contains 485 mg. of $MgBr_2$ per ml. at 25° was used.

Exchange Reactions.—The concentrated magnesium bromide solution and the concentrated diethylmagnesium solution were added to a sufficient volume of ether to yield a solution 0.5 molar in each component (1.0 molar in magnesium). This was permitted to stand for various time periods, and then 1.5 mole equivalents of 1,4-dioxane was added slowly over a 15-minute period with constant agitation. The suspension was agitated slowly for 15 minutes and then centrifuged at 2000 r.p.m. for five minutes. The supernatant solution was analyzed for basic magnesium using the technique described by Gilman[10] and was found to be approximately 0.5 *M* in magnesium. A potentiometric titration for halogen indicated that the supernatant liquid was approximately 0.01 *M* in bromine.[11]

Sampling and Counting.—A portion of the supernatant liquid was transferred to a glass planchet, air hydrolyzed, treated with concentrated hydrobromic acid and dried. A similar planchet was prepared from the original magnesium bromide solution.

The activity of the samples was determined using an Amperex Type 200 CB halogen filled Geiger tube. The activity of the samples was followed for 60 hr. A plot of log(activity) *versus* time indicated high radiochemical purity and a $t_{0.5}$ of 21.2 hr. The reported $t_{0.5}$ of Mg^{28} is 21.25 hr.[12]

Acknowledgment.—The authors are indebted to the staff and crew of the Carnegie Institute of Technology Synchrocyclotron at Saxonburg, Pennsylvania, for their aid and coöperation.

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[6] A. B. Garrett, Arthur Sweet, Wm. L. Marshall, David Riley and Anis Touma, *Rec. Chem. Progr.*, **13**, 155 (1952).

[7] J. H. Wotiz, C. A. Hollingsworth and Raymond E. Dessy, THIS JOURNAL, **78**, 1221 (1956).

[8] M. Lindner, *Phys. Rev.*, **89**, 1150 (1953).

[9] W. E. Doering and C. R. Noller, THIS JOURNAL, **61**, 3436 (1939).

[10] H. Gilman, *ibid.*, **51**, 1576 (1929).

[11] It was very difficult to obtain reliable data on the halogen concentration in the solutions when only one-ml. samples were available. However, determinations made during blank runs which did not involve the radioactive tracer and hence could be run on a larger scale indicated similar results.

[12] G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1955.

PITTSBURGH, PENNA.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Condensation of Grignard Reagents with 3-Pyridyl and 3-Quinolyl Ketones

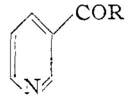
BY REYNOLD C. FUSON AND JOHN J. MILLER

RECEIVED JANUARY 18, 1957

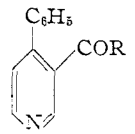
Phenylmagnesium bromide was found to condense in the 1,4-manner with 3-benzoyl-, 3-mesitoyl- and 3-duroylpyridine and with 3-benzoyl- and 3-mesitoylquinoline. Benzylmagnesium chloride reacted in a similar way with the hindered pyridyl ketones, but gave the 1,2-addition product with 3-benzoylpyridine. The products with the phenyl reagents were the corresponding dihydro aromatic compounds; they were dehydrogenated readily with chloranil. 2-Azafluorenone (III) was produced when either 3-mesitoyl-4-phenylpyridine or 3-duroyl-4-phenylpyridine was treated with polyphosphoric acid. The action of polyphosphoric acid on 3-mesitoyl-4-phenylquinoline provided 3,4-benzo-2-azafluorenone (X).

In a search for diaryl ketones that might be unusually receptive to conjugate attack by Grignard reagents, attention was directed to the 3-pyridyl ketones. That these compounds would undergo condensation with organomagnesium halides in the 1,4-manner was indicated clearly by the observation of Frank and Weatherbee,[1] that *n*-propylmagnesium bromide reacted with nicotinonitrile to give *n*-propyl 4-*n*-propyl-3-pyridyl ketone.

In the present work it was found that 3-duroylpyridine (Ia) reacted with phenylmagnesium bromide to yield a light yellow solid, the infrared spectrum of which indicates the presence of an >NH group, consistent with the structure of a dihydro phenyl substituted 3-duroylpyridine. The yield was 88% of theoretical. Dehydrogenation of the dihydro compound with chloranil gave 3-duroyl-4-phenylpyridine (IIa) in nearly quantitative yield.



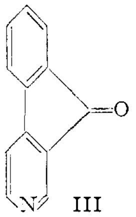
Ia, R = Dur
b, R = Mes



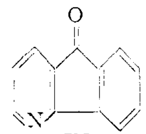
IIa, R = Dur
b, R = Mes

Similar results were obtained with 3-mesitoylpyridine (Ib). The dihydro compound, isolated in a yield of 63%, underwent dehydrogenation smoothly with chloranil to give 3-mesitoyl-4-phenylpyridine (IIb).

The possibility existed that the products of the above reactions were pyridines phenylated in the 2- rather than the 4-position. That the materials were substituted in the 4-position was proved by the isolation of 2-azafluorenone (III) from the reaction of either phenylated ketone (IIa or IIb) with polyphosphoric acid.[2] 4-Azafluorenone (IV) would have been produced if the ketones had been phenylated in the 2-position.



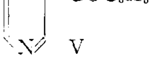
III



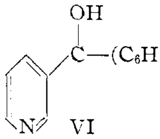
IV

It is assumed that the 2-azafluorenone (III) is obtained by cyclization of 4-phenylnicotinic acid, the product which would be expected from cleavage of the ketones with polyphosphoric acid.

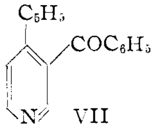
As might have been anticipated from the work of Frank and Weatherbee, conjugate addition was realized also with the unhindered ketone, 3-benzoylpyridine (V). Treatment of this material with phenylmagnesium bromide gave rise to diphenyl-3-pyridylcarbinol (VI), the 1,2-addition product, in 22% yield and to a dihydro 1,4-addition product in a yield of 45%. Dehydrogenation of this conjugate addition product gave 4-phenyl-3-benzoylpyridine (VII).



V

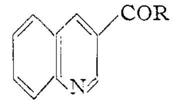


VI

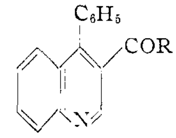


VII

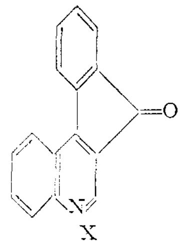
It was thought that conjugate addition to ketones in the quinoline series would be even more facile than to those in the pyridine series. This expectation was borne out by the addition of phenylmagnesium bromide to 3-benzoylquinoline (VIIIa) A dihydro derivative of 3-benzoyl-4-phenylquinoline was isolated in a yield of 90%. Dehydrogenation to 3-benzoyl-4-phenylquinoline (IXa) was accomplished with chloranil.



VIIIa, R = C_6H_5
b, R = Mes



IXa, R = C_6H_5
b, R = Mes



X

The addition of the phenyl reagent to 3-mesitoylquinoline (VIIIb) gave the expected dihydro derivative, which was aromatized to 4-phenyl-3-mesitoylquinoline (IXb) in excellent yield. Cleavage of this hindered ketone with polyphosphoric acid provided 3,4-benzo-2-azafluorenone (X).

The 3-pyridyl ketones were synthesized by the method of Friedel and Crafts. Nicotinyl chloride hydrochloride, prepared by the action of thionyl chloride on nicotinic acid,[3] was used with benzene and mesitylene, respectively, in the synthesis of 3-benzoyl- and 3-mesitoylpyridine. It was found necessary to employ free nicotinyl chloride[4] in tetrachloroethane as a solvent for the preparation of 3-duroylpyridine. 3-Benzoylquinoline, which has not been described previously, was obtained in 65% yield from the corresponding free acid chloride. 3-Mesitoylquinoline was prepared by treatment of the corresponding acid chloride hydrochloride with mesitylene and aluminum chloride in carbon disulfide.

The action of benzylmagnesium chloride on 3-benzoylpyridine proved interesting in that no conjugate addition product was isolated. It has been observed in many cases that the benzyl reagent brings about 1,2- rather than 1,4-addition even with hindered ketones.[5] With 3-mesitoylpyridine, the benzyl reagent produced a yellow solid, which, on the basis of infrared and combustion analyses, was assigned the structure of a dihydro-4-benzyl-3-mesitoylpyridine. Dehydrogenation of this material has not been accomplished. The position of the double bonds in this and other dihydro compounds has not been established definitely. The reaction of the benzyl reagent with 3-benzoylquinoline also proceeded in the conjugate manner.

Experimental[6]

3-Mesitoylpyridine (Ib).—To the nicotinyl chloride hy-

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[1] R. L. Frank and C. Weatherbee, THIS JOURNAL, **70**, 3842 (1948).

[2] G. Nowlin, *ibid.*, **72**, 5754 (1950).

[3] F. J. Villani, M. S. King and D. Papa, *J. Org. Chem.*, **17**, 249 (1952).

[4] H. N. Wingfield, Jr., W. R. Harlan and H. R. Hammer, THIS JOURNAL, **75**, 4364 (1953).

[5] W. G. Young and J. D. Roberts, *ibid.*, **66**, 2131 (1944).

[6] All melting points are corrected.

drochloride, produced by the action of excess thionyl chloride on 85.5 g. (0.7 mole) of nicotinic acid, was added 500 ml. of mesitylene. The mixture was cooled in an ice–salt-bath, and 348 g. (2.6 moles) of aluminum chloride was introduced in small amounts. The deep red solution was heated on a steam-bath for 6 hr. and then decomposed with ice and hydrochloric acid. Addition of an excess of sodium hydroxide to the aqueous layer caused the separation of a brown oil, which was extracted by shaking the mixture successively with five 100-ml. portions of chloroform. The chloroform extracts were combined, washed with water and dried over sodium sulfate. Evaporation of the solvent left a brown oil. Distillation of this material under reduced pressure gave 79 g. (50.5%) of 3-mesitoylpyridine, a light yellow oil, b.p. 96–98° (0.1 mm.).

Anal.[7] Calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.13; H, 6.72; N, 6.32.

The infrared spectrum[8] of the oil supports the proposed structure. Absorption bands assignable to a hindered, conjugated carbonyl group (1675 cm.$^{-1}$) and to the mesitylene group (850 cm.$^{-1}$) are present.

The picrate of the ketone crystallized from ethanol in yellow needles, m.p. 167–168°.

Anal. Calcd. for $C_{21}H_{18}N_4O_8$: C, 55.51; H, 3.99; N, 12.33. Found: C, 55.79; H, 4.07; N, 12.36.

Dihydro-3-mesitoyl-4-phenylpyridine.—To the Grignard reagent prepared from 16.84 g. (0.1072 mole) of bromobenzene and 2.61 g. (0.1072 g. atom) of magnesium was added 12.08 g. (0.0536 mole) of 3-mesitoylpyridine. The addition was completed in 10 min. The yellow solid, which formed in the solution while the ketone was being added, changed to a brown gum as the reaction mixture was stirred for 10 min. Saturated ammonium chloride solution was introduced, and the yellow solid which separated was collected on a filter. Evaporation of the ether left additional yellow material, m.p. 174–181°. Recrystallization from ethanol gave 10.22 g. (63%) of a light yellow powder, m.p. 182–188°. Vacuum sublimation or recrystallization did not decrease the melting range.

An absorption band assignable to an N—H stretching frequency (3260 cm.$^{-1}$) is present in the infrared spectrum. The intensity of the carbonyl band (1668 cm.$^{-1}$) is extremely low. The structure proposed is a dihydro-3-mesitoyl-4-phenylpyridine.

Anal. Calcd. for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 82.90; H, 7.20; N, 4.43.

3-Mesitoyl-4-phenylpyridine (IIb).—Benzene solutions of 3.03 g. (0.01 mole) of dihydro-3-mesitoyl-4-phenylpyridine and 2.46 g. (0.01 mole) of chloranil were mixed in a 500-ml., round-bottomed flask. The mixture was heated at the reflux temperature for 8 hr. and then allowed to cool. Extraction of the solution with five 100-ml. portions of 10% aqueous sodium hydroxide removed 1.83 g. of tetrachlorohydroquinone. A brown oil (2.3 g.), which was left when the benzene was evaporated, was crystallized from an ethanol–water mixture. Vacuum sublimation of this crude material at 95° (0.05 mm.) gave white prisms, m.p. 94–95.2° (77% yield).

Anal. Calcd. for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.91; H, 6.20; N, 4.67.

The return of the carbonyl band (1668 cm.$^{-1}$) to normal intensity in the infrared spectrum is striking.

3-Duroylpyridine (Ia).—Nicotinyl chloride was prepared by the method of Wingfield, Harlan and Hammer[4] from 32.2 g. (0.2 mole) of potassium nicotinate and 25.2 g. (0.2 mole) of oxalyl chloride. Two hundred and fifty grams of tetrachloroethane was added to the acid chloride, and 22.8 g. (0.17 mole) of durene was then introduced. The mixture was cooled in an ice–salt-bath, and 50 g. (0.38 mole) of aluminum chloride was added in small portions. The solution was allowed to come to room temperature and was then heated on a steam-bath for 5 hr. The mixture was decomposed with ice and hydrochloric acid, and the organic layer was subjected to steam distillation to remove the tetrachloroethane. The ketone was extracted from the brown, tarry residue with low-boiling petroleum ether. The brown solution, after repeated treatment with decolorizing carbon and evaporation of the solvent, gave 3-duroylpyridine in the form of colorless plates. After recrystallization from low-boiling petroleum ether, the product weighed 13.93 g. (32% yield), m.p. 80.5–81.5°.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.37; H, 7.15; N, 5.90.

The picrate was prepared and purified by recrystallization from ethanol, m.p. 183–185°.

Anal. Calcd. for $C_{22}H_{20}N_4O_8$: C, 56.41; H, 4.30; N, 11.96. Found: C, 56.66; H, 4.17; N, 11.92.

Dihydro-3-duroyl-4-phenylpyridine.—Phenylmagnesium bromide, prepared from 3.93 g. (0.025 mole) of bromobenzene and 0.608 g. (0.025 g. atom) of magnesium, was added to 2.99 g. (0.0125 mole) of 3-duroylpyridine. The subsequent procedure was similar to that described for the mesitoyl compound. The dihydro-3-duroyl-4-phenylpyridine, a yellow solid, m.p. 198–207°, was obtained in 88% yield.

Anal. Calcd. for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41. Found: C, 82.97; H, 7.19; N, 4.34.

The infrared spectrum is similar to that of dihydro-3-mesitoyl-4-phenylpyridine; the carbonyl group absorption is again very weak.

3-Duroyl-4-phenylpyridine (IIa).—Treatment of 0.4 g. (0.0012 mole) of dihydro-3-duroyl-4-phenylpyridine with 0.295 g. (0.0012 mole) of chloranil provided 0.39 g. (99%) of the aromatized product, 3-duroyl-4-phenylpyridine, m.p. 168–169.5°.

Anal. Calcd. for $C_{22}H_{21}NO$: C, 83.77; H, 6.71; N, 4.44. Found: C, 83.51; H, 6.71; N, 4.29.

The picrate, m.p. 214–215°, was recrystallized from ethanol.

Anal. Calcd. for $C_{28}H_{24}N_4O_8$: C, 61.76; H, 4.44; N, 10.29. Found: C, 61.58; H, 4.52; N, 10.21.

3-Benzoylpyridine (V).—This ketone was prepared from nicotinic acid in a yield of 87.5% by the method of Villani, King and Papa.[3] The boiling point is 154–156° at 2.5–2.7 mm. **The picrate**, after recrystallization from ethanol, melted at 163–165°; reported 164–166°[3] and 161°.[9]

Dihydro-3-benzoyl-4-phenylpyridine and Diphenyl-3-pyridylcarbinol (VI).—The addition of 4 g. (0.022 mole) of 3-benzoylpyridine to the Grignard reagent prepared from 7.22 g. (0.046 mole) of bromobenzene and 1.09 g. (0.045 g. atom) of magnesium was followed in 20 min. by hydrolysis with saturated ammonium chloride solution. When the ethereal layer was concentrated, a yellow solid and a tan oil were obtained. Recrystallization of the solid from a large volume of ether gave 2.57 g. (45% yield) of dihydro-3-benzoyl-4-phenylpyridine, m.p. 142–148°. Vacuum sublimation of the yellow plates at 140° (0.1 mm.) provided a solid melting at 147–150°.

Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.94; H, 6.07; N, 5.30.

The oil obtained from the reaction crystallized from ether. Recrystallization from ethyl acetate gave 1.27 g. (22% yield) of lustrous, white plates of diphenyl-3-pyridylcarbinol, m.p. 115–116°, reported[10] 115–116°.

Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.74; H, 5.89; N, 5.37.

The melting point of the **picrate** of this carbinol, m.p. 195–197°, agrees with that reported.[10]

3-Benzoyl-4-phenylpyridine (VII).—Dehydrogenation of the corresponding dihydro compound with chloranil gave 3-benzoyl-4-phenylpyridine in a yield of 83%, m.p. 89.5–90°.

Anal. Calcd. for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.36; H, 5.08; N, 5.29.

The picrate, m.p. 203–205°, crystallized from ethanol.

Anal. Calcd. for $C_{24}H_{16}N_4O_8$: C, 59.02; H, 3.30; N, 11.47. Found: C, 59.11; H, 3.46; N, 11.23.

2-Azafluorenone (III).—A mixture of an excess of polyphosphoric acid and 0.5 g. of 3-mesitoyl-4-phenylpyridine was heated with stirring for 1.5 hr. at 185–200° (25 mm.) in a flask equipped for downward distillation. When the dark brown oil, produced in the reaction flask, was poured

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(7) Microanalyses were performed by Mr. Joseph Nemeth, Mrs. R. Maria Benassi, Mrs. Lucy Chang, Mrs. Ruby Ju, Mr. Rollo Nesset and Miss Claire Higham.

(8) The infrared data were obtained and interpreted by Mr. James Brader, Mrs. Louise Griffing and Mr. Sy Portnow.

(9) F. B. LaForge, THIS JOURNAL, **50**, 2477 (1928).

(10) L. C. Anderson and N. V. Seeger, *ibid.*, **71**, 343 (1949).

on ice, an orange solution formed. The solution was filtered and neutralized with 5% sodium hydroxide. An orange solid, 2-azafluorenone, precipitated (48% yield). Vacuum sublimation of the solid gave yellow plates, m.p. 155.5–156.5°. The melting points reported for 2-azafluorenone are 156–158°[11] and 130°.[12]

The infrared spectrum of a Nujol mull of the material contains bands assignable to a carbonyl group of the fluorenone type (1707 cm.$^{-1}$) and to an *o*-disubstituted benzene ring (735 cm.$^{-1}$). The carbonyl band is at 1720 cm.$^{-1}$ in 5% chloroform solution.

Anal. Calcd. for $C_{12}H_7NO$: C, 79.55; H, 3.89; N, 7.73. Found: C, 79.46; H, 4.01; N, 7.88.

Treatment of 3-duroyl-4-phenylpyridine with polyphosphoric acid gave the same product.

3-Bromoquinoline.—Quinoline hydrobromide perbromide was pyrolyzed to 3-bromoquinoline hydrobromide in 36.5% yield according to the method of Claus and Collischon.[13] The amine was liberated quantitatively by treatment with base.

3-Quinolinecarboxylic Acid.—Treatment of 3-bromoquinoline with cuprous cyanide provided 3-cyanoquinoline, m.p. 106–107°, in a 60% yield.[14] Hydrolysis of the nitrile gave the acid, m.p. 272–273°, in 89% yield.[15]

3-Benzoylquinoline (VIIIa).—The potassium salt of 3-quinolinecarboxylic acid was treated with oxalyl chloride, and the acid chloride produced was condensed with benzene and aluminum chloride according to the method for the preparation of 3-duroylpyridine. 3-Benzoylquinoline, m.p. 76–77°, was isolated in 65% yield.

Anal. Calcd. for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.01. Found: C, 82.51; H, 4.70; N, 6.04.

The picrate, m.p. 216–218°, was recrystallized from ethanol.

Anal. Calcd. for $C_{22}H_{14}N_4O_8$: C, 57.15; H, 3.05; N, 12.12. Found: C, 57.01; H, 3.06; N, 12.02.

Dihydro-3-benzoyl-4-phenylquinoline.—The reaction of 1.81 g. (0.0078 mole) of 3-benzoylquinoline with phenylmagnesium bromide, prepared from 2.48 g. (0.0158 mole) of bromobenzene and 0.384 g. (0.0158 g. atom) of magnesium, gave 2.17 g. (90% yield) of dihydro-3-benzoyl-4-phenylquinoline, m.p. 201–204°.

Anal. Calcd. for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50. Found: C, 84.58; H, 5.51; N, 4.44.

3-Benzoyl-4-phenylquinoline (IXa).—Dehydrogenation of 0.31 g. (0.001 mole) of dihydro-3-benzoyl-4-phenylquinoline with 0.25 g. (0.001 mole) of chloranil gave 0.23 g. (75% yield) of 3-benzoyl-4-phenylquinoline, m.p. 115–116°.

Anal. Calcd. for $C_{22}H_{15}NO$: C, 85.41; H, 4.89; N, 4.53. Found: C, 85.12; H, 5.19; N, 4.33.

3-Mesitoylquinoline (VIIIb).—3-Quinolinecarboxylic acid chloride hydrochloride was prepared from 3 g. (0.0173 mole) of 3-quinolinecarboxylic acid and excess thionyl chloride. After the excess thionyl chloride was removed by vacuum distillation, 150 ml. of carbon disulfide, 2.1 g. (0.0174 mole) of mesitylene and 4.62 g. (0.0346 mole) of aluminum chloride was introduced and the mixture was stirred at room temperature for 19 hr. Decomposition of the mixture was accomplished with ice and hydrochloric acid. The aqueous layer was made basic with sodium hydroxide and extracted with ether. Removal of the ether by distillation left 1.76 g. (37% yield) of a yellow-white solid, m.p. 87–91°. Vacuum sublimation gave white crystals of 3-mesitoylquinoline, m.p. 90.5–92°.

Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 83.06; H, 6.29; N, 5.07.

Dihydro-4-phenyl-3-mesitoylquinoline.—Treatment of 1 g. (0.0036 mole) of 3-mesitoylquinoline with the Grignard reagent prepared from 0.175 g. (0.0072 g. atom) of magnesium and 1.13 g. (0.0072 mole) of bromobenzene gave 1.07 g. (84.5% yield) of a dihydro-4-phenyl-3-mesitoylquinoline. A sublimed sample exhibited a melting range of 268–274°.

Anal. Calcd. for $C_{25}H_{23}NO$: C, 84.95; H, 6.56; N, 3.96. Found: C, 84.78; H, 6.48; N, 3.95.

4-Phenyl-3-mesitoylquinoline (IXb).—Dehydrogenation of 0.75 g. (0.002 mole) of dihydro-4-phenyl-3-mesitoylquinoline was accomplished with 0.49 g. (0.002 mole) of chloranil to give 0.65 g. (92.5% yield) of 4-phenyl-3-mesitoylquinoline, m.p. 98.5–100°.

Anal. Calcd. for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.55; H, 5.97; N, 3.98.

3,4-Benzo-1-azafluorenone (X).—The procedure described for the preparation of 2-azafluorenone was followed. The ketone was obtained in 55.7% yield from 4-phenyl-3-mesitoylquinoline. Recrystallization from ethanol gave yellow needles, m.p. 223–224°, reported[16] 216–217°.

Anal. Calcd. for $C_{16}H_9NO$: C, 83.10; H, 3.92; N, 6.06. Found: C, 83.25; H, 3.74; N, 5.93.

The 2,4-dinitrophenylhydrazone of 3,4-benzo-2-azafluorenone, crystallized from ethanol, melted at 293° dec., reported[16] 290° dec.

Dihydro-4-benzyl-3-mesitoylpyridine.—A yellow solid, dihydro-4-benzyl-3-mesitoylpyridine, m.p. 169–172°, was obtained in 32% yield when 3-mesitoylpyridine was treated with benzylmagnesium chloride. The conditions employed were the same as those described in the other Grignard reactions. The infrared spectrum of the dihydro compound is similar to that of the corresponding phenyl compound.

Anal. Calcd. for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41. Found: C, 82.71; H, 7.29; N, 4.67.

Benzylphenyl-3-pyridylcarbinol.—The introduction of 1.83 g. (0.01 mole) of 3-benzoylpyridine to a solution of benzylmagnesium chloride, prepared from 0.535 g. (0.022 g. atom) of magnesium and 2.77 g. (0.022 mole) of benzyl chloride, followed by hydrolysis with hydrochloric acid provided 1.5 g. of a colorless solid, m.p. 240–241° dec. The infrared spectrum contains a band at 2100 cm.$^{-1}$ which indicates the presence of a hydrochloride. A silver nitrate test confirmed the presence of halogen.

Anal. Calcd. for $C_{19}H_{18}ClNO$: C, 73.19; H, 5.82; N, 4.49. Found: C, 72.72; H, 5.55; N, 4.34.

Treatment of the hydrochloride with 5% aqueous sodium hydroxide gave almost quantitative liberation of benzylphenyl-3-pyridylcarbinol as white plates, m.p. 154–155°. The over-all yield was 48.5%.

Anal. Calcd. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.82; H, 6.32; N, 5.02.

Dihydro-4-benzyl-3-benzoylquinoline.—The action of the benzyl Grignard reagent, prepared from 1.34 g. (0.0106 mole) of benzyl chloride and 0.26 g. (0.0106 g. atom) of magnesium, on 1.23 g. (0.0053 mole) of 3-benzoylquinoline gave a brown oil from which 0.22 g. of a yellow solid, m.p. 195–200°, was obtained. The structure dihydro-4-benzyl-3-benzoylquinoline was assigned on the basis of the similarity of the infrared spectrum to that of dihydro-4-benzyl-3-mesitoylpyridine.

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