

Calcd. for $C_{12}H_{12}ONCl_3$: C, 51.26; H, 3.97. Found: C, 51.02; H, 4.11.

Hydrolysis of Chloral-2-ethylquinoline.—This hydrolysis was conducted using the same molar proportions and conditions as those used for chloral-quinaldine.

Five hundredths of a mole of the adduct was warmed with 67 ml. of ethanol, and 56 ml. of water was added slowly. The mixture was heated to boiling, and to it was added, as quickly as the vigorous ebullition would permit, a solution of 11.7 g. of sodium hydroxide in 37 ml. of water. After the reaction had subsided the solution was kept hot for five minutes and 100 ml. of hot ethanol was added. After the mixture had cooled overnight, no crystalline product had separated, so the solvents were removed *in*

vacuo, and the residue was dissolved in water. The product was precipitated with 11 ml. of concd. hydrochloric acid and 5 ml. of acetic acid: yield, 79%, m. p. 190–195° (dec.). Recrystallization from dilute dioxane gave the colorless β -2-quinolyicrotonic acid, m. p. 204–206° (dec.). *Anal.* Calcd. for $C_{12}H_{11}O_2N$: C, 73.22; H, 5.20. Found: C, 72.85; H, 5.18.

Summary

The action of alcoholic sodium hydroxide on chloral-quinaldine gives 3-acetyl-1,2-dihydroquinoline-2-carboxylic acid.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reaction of Benzophenone β -Naphthyl with Phenylmagnesium Bromide and with Phenyllithium

BY HENRY GILMAN AND JOHN MORTON

The forced reaction of phenylmagnesium bromide with benzophenone anil was reported earlier from this Laboratory.¹ It was found that the Grignard reagent undergoes a lateral-nuclear 1,4 addition to the conjugated system consisting of the anil linkage and an unsaturated linkage of one benzohydrylidene phenyl group to produce, after hydrolysis and a hydrogen shift, *o*-phenylbenzohydrylaniline. Similar lateral-nuclear additions, in which Grignard reagents add 1,4 to ketones whose carbonyl groups are conjugated with unsaturated linkages in aromatic nuclei, have since been described²; also, it has been demonstrated that benzalquinaldine adds phenylmagnesium bromide in a lateral-nuclear sense.³

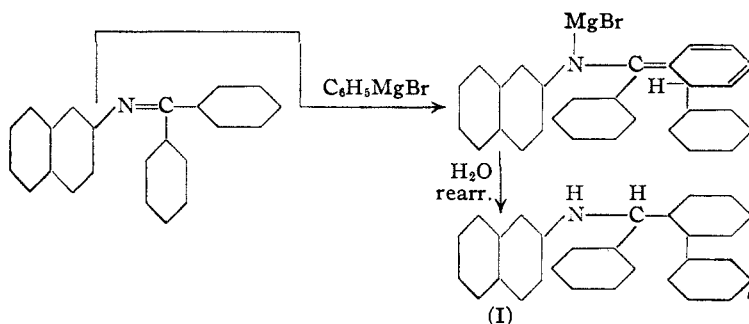
Further work in this Laboratory⁴ established that phenyllithium adds to benzophenone anil at the anil linkage only, yielding triphenylmethylaniline. This reaction proceeds at the temperature of refluxing ether, whereas phenylmagnesium bromide has no detectable effect upon the anil at this temperature.

The present study of the reaction of benzophenone β -naphthyl with phenylmagnesium bromide and with phenyllithium, has been carried out to discover whether the substitution of an N- β -naphthyl group for the N-phenyl group of benzophenone anil could affect the course of reaction with either of the organometallic compounds, and

particularly whether any addition involving the naphthyl group itself could be observed.

We find that the naphthyl behaves quite similarly to the anil with respect to both organometallic compounds. With phenylmagnesium bromide at the temperature of refluxing ether, no reaction occurs; when ether-toluene is used and the temperature is raised to 90–100°, a compound melting at 185–186° and having a nitrogen content corresponding to that of *o*-phenylbenzohydryl- β -naphthylamine (I) is obtained in pure yields as high as 71%. Like the similarly substituted aniline described earlier,¹ this substance yields 9-phenylfluorene when refluxed with alcoholic hydrochloric acid.

The compound melting at 185–186° has been shown to be identical with the product of the



forced reaction between *o*-biphenylmagnesium iodide and benzal- β -naphthylamine, and was thus identified as (I). The reaction leading to the formation of compound (I) from the naphthyl is shown.

We find that phenyllithium, on the other hand, reacts with the naphthyl at the temperature of refluxing ether to produce a compound which melts at 185° but which gives a large depression of melting point when mixed with (I). The product from the RLi reaction proved to be identical with the product of the condensation of triphenylcarbinol with β -naphthylamine in glacial acetic acid. The

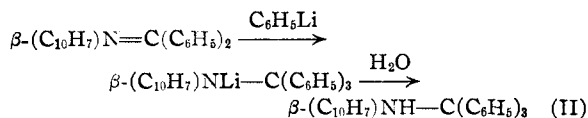
(1) Gilman, Kirby and Kinney, *THIS JOURNAL*, **51**, 2252 (1929).

(2) Kohler and Nygaard, *ibid.*, **52**, 4128 (1930); Allen and Overbaugh, *ibid.*, **57**, 1322 (1935); Koelsch and Rosenwald, *ibid.*, **59**, 2166 (1938); Lutz and Reveley, *ibid.*, **63**, 3178 (1941); Geissman and Morris, *ibid.*, **66**, 716 (1944); Fuson, McKusick and Spangler, *ibid.*, **67**, 597 (1945); Koelsch and Rosenwald, *J. Org. Chem.*, **3**, 462 (1938); Koelsch and Anthes, *ibid.*, **6**, 558 (1941); Fuson, Kaiser and Speck, *ibid.*, **6**, 845 (1941); Fuson, Armstrong and Speck, *ibid.*, **7**, 297 (1942).

(3) Hoffman, Farlow and Fuson, *THIS JOURNAL*, **55**, 2000 (1933).

(4) Gilman and Kirby, *ibid.*, **55**, 1625 (1933).

product, then, must be triphenylmethyl- β -naphthylamine (II), and its formation from the naphthil must proceed as follows



The pure yield is 72.5%.

Experimental

Preparation of Benzophenone β -Naphthil.—The preparation of this compound given by Reddelien⁵ was modified as follows: 143 g. (0.56 mole) of benzophenone anil was heated with 148 g. (1.03 mole) β -naphthylamine in a flask equipped with a downward condenser and evacuated to 20 mm. Heat was applied with a strong, direct Bunsen flame. After a considerable quantity of aniline had distilled over, solid β -naphthylamine began to appear in the receiver, whereupon the heating was stopped. The reaction mixture solidified on cooling. Two recrystallizations of this solid from absolute ethanol gave 110 g. (64%) of greenish crystals melting at 96–97°.

Reaction of Phenylmagnesium Bromide with Benzophenone β -Naphthil.—Two-tenths mole of phenylmagnesium bromide in ether was added to 15.5 g. (0.05 mole) of benzophenone β -naphthil in toluene. There was no observable reaction during the addition. The solution was partly freed of ether by raising the temperature to 90–100°, and was stirred for ten hours at the elevated temperature. The mixture was then cooled and hydrolyzed with iced ammoniacal ammonium chloride, and the ether-toluene layer was separated and steam-distilled. The light-colored residue weighed 14–16 g. (71–82%) and generally melted between 175 and 180°. Solution of this material in boiling ethanol-toluene and subsequent extended cooling yielded 10.5–14 g. (51–71%) of pure white powder melting at 185–186°. In one case, there appeared a small amount (approx. 0.5 g.) of a resinous material which separated from the alcohol-toluene some weeks after the amine had crystallized. The composition of this substance has not as yet been determined.

Anal. Calcd. for $\text{C}_{29}\text{H}_{23}\text{N}$: N, 3.62. Found: N, 3.45, 3.87.

Cleavage of *o*-Phenylbenzohydril- β -naphthylamine and of Triphenylmethyl- β -naphthylamine.—One gram of (I) was refluxed for seventeen hours in a mixture of 10 cc. of concentrated hydrochloric acid and 30 cc. of 95% ethanol. The solution was evaporated and the solid residue treated with dilute hydrochloric acid to remove amines. The remaining solid was recrystallized from 95% ethanol to give 0.21 g. (34%) of 9-phenylfluorene, and β -naphthylamine. Triphenylmethyl- β -naphthylamine (1 g.) cleaved under the same conditions to give 0.33 g. (53%) of triphenylmethane, and β -naphthylamine. The identities of the cleavage products were established by comparison with authentic specimens.

Reaction of *o*-Biphenylmagnesium Iodide with Benzal- β -naphthylamine.—Thirty grams (0.1 mole) of *o*-iodo-

(5) Reddelien, *Ber.*, **54**, 3121 (1921).

biphenyl¹ in dry ether was added to 5 g. (0.2 atom) of magnesium turnings. Activated copper-magnesium alloy⁶ was used to start the reaction, which proceeded smoothly with the formation of 0.074 mole (74%) of Grignard reagent. The resulting solution was added to a solution of 17.1 g. (0.074 mole) of benzal- β -naphthylamine⁷ in toluene. Ether was distilled off until the temperature reached 90°, and the solution was stirred at this temperature for eight hours. The mixture was hydrolyzed with dilute hydrochloric acid, and the toluene layer was separated and steam-distilled. The tarry residue from this process was dissolved in hot ethanol-toluene, and this solution, after lengthy cooling, deposited 2.5 g. (8.8%) of salmon-colored crystals melting at 182–184°. Another recrystallization from the same solvent yielded 2.0 g. (7%) of almost colorless crystals melting at 185–186°. This melting point is not depressed by mixture with the compound obtained from benzophenone β -naphthil and phenylmagnesium bromide.

Reaction of Benzophenone β -Naphthil with Phenyllithium.—Twenty-three grams (0.075 mole) of the naphthil in ether was treated with 0.08 mole of phenyllithium in ether. Gentle spontaneous refluxing occurred as the solutions were mixed. After being stirred for six hours at reflux, the solution was hydrolyzed with water. Just prior to hydrolysis, the solution gave a positive Color Test I.⁸ The ethereal layer was separated, washed with water, and steam-distilled. Twenty-four grams (84%) of greenish-white residue melting at 176–178° was obtained. This was recrystallized from ethanol-toluene to give 21 g. (72.5%) of white crystals melting at 185–186° but giving a large depression of this melting point when mixed with (I).

Anal. Calcd. for $\text{C}_{29}\text{H}_{23}\text{N}$: N, 3.62. Found: N, 3.50.

Condensation of β -Naphthylamine with Triphenylcarbinol.—In this reaction, modeled after the synthesis of the similarly substituted aniline given by Baeyer and Villiger,⁹ 5 g. of triphenylcarbinol and 10 g. of β -naphthylamine were refluxed for one-half hour in glacial acetic acid. The solution was cooled and diluted with water, whereupon a white precipitate appeared. This was filtered off and washed with 95% ethanol, leaving a powdery residue which, when recrystallized from watered acetone, weighed 0.1 g. (1.3%) and melted at 185–186°. A mixed melting point with the material from the phenyllithium reaction showed no depression.

Summary

Benzophenone β -naphthil undergoes a lateral-nuclear 1,4 addition with phenylmagnesium bromide under forced conditions, yielding *o*-phenylbenzohydril- β -naphthylamine. The same naphthil undergoes 1,2 addition with phenyllithium under mild conditions, to yield triphenylmethyl- β -naphthylamine.

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(6) Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1928).

(7) Claisen, *Ann.*, **237**, 273 (1887).

(8) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

(9) Baeyer and Villiger, *Ber.*, **35**, 3016 (1902).