233. *The Interaction of Phenylmagnesium Bromide with 1-Chloropiperidine and Other* N-*Chloro-compounds.*

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SINCE Coleman and Hauser (*J. Amer. Chem. Soc.*, 1928, **50**, 1193) have found that a variety of Grignard reagents (including phenylmagnesium bromide) react under the usual conditions with monochloroamine at 0° to give 80—90% yields of the corresponding primary amine, the reaction between 1-chloropiperidine and phenylmagnesium bromide (this vol., p. 1378) has been re-examined. No 1-phenylpiperidine was obtained, the two main products being benzene and chlorobenzene; piperidine was isolated from the aqueous solution:

$$C_5H_{10}NCl + PhMgBr \longrightarrow PhCl + C_5H_{10}N{\cdot}MgBr \xrightarrow{H_2O} C_5H_{11}N + MgBr{\cdot}OH$$

$$PhMgBr + H_2O \longrightarrow C_6H_6 + MgBr{\cdot}OH$$

Dimethyl- and diethyl-chloroamines react in the same sense with phenylmagnesium bromide, chlorobenzene and the secondary base being formed to a large extent, but no dialkylaniline. (Diethyliodoamine is stated by Buylla, *Chem. Abstr.*, 1911, 3802, to be without action on ethylmagnesium bromide.) Similarly from chloramine-T (and dichloramine-T) and phenylmagnesium bromide solutions, chlorobenzene has been isolated. Chlorobenzene has also been identified as an overlooked product of the reaction between phenylmagnesium bromide or iodide and nitrogen trichloride in benzene solution described by Strecker (*Ber.*, 1910, **43**, 1131):

$$3PhMgBr + NCl_3 \longrightarrow 3PhCl + NH_3 + 3MgBr{\cdot}OH$$

It has been found that, in addition to aniline (Coleman and Hauser, *loc. cit.*), an appreciable quantity of chlorobenzene is formed in the reaction between monochloroamine and phenylmagnesium bromide.

It is therefore evident that chlorobenzene is generally formed during reactions between *N*-chloro-compounds and phenylmagnesium bromide—these thus being another series of interactions where a "positive" chlorine effect is important.

EXPERIMENTAL.

Reaction of Phenylmagnesium Bromide with N-*Chloro-compounds.*—The Grignard solution was prepared from equivalent quantities of bromobenzene and magnesium in ether and cooled to 0° and an ethereal solution of the chloro-compound was run in slowly. If the reaction was vigorous the mixture was kept for 12 hours, in other cases it was refluxed for ½—2½ hours, before being cooled and decomposed with ammonium chloride solution. The ethereal layer was then dried and fractionated. The chlorobenzene produced was in each case identified by conversion into 2 : 4-dinitrochlorobenzene, m. p. and mixed m. p. 52°.

(1) *With* 1-*chloropiperidine.* The reaction between the Grignard solution (bromobenzene, 62 g.; ether, 300 c.c.) and 1-chloropiperidine (42 c.c. in 80 c.c. of ether) was very vigorous. Piperidine was obtained from the basified aqueous sludge by steam distillation and identified as the hydrochloride, m. p. 237°, and *p*-toluenesulphonyl derivative, m. p. 101—102°. The ethereal solution gave the following fractions: (a) 8 g., b. p. 79—81°, identified as benzene by b. p. and nitration to *m*-dinitrobenzene; (b) 9 g., b. p. 127—128°; (c) 12 g., b. p. 128—131°; (d) 1·5 g., b. p. 132—200°, not examined; (e) 2·5 g., b. p. 200—250°, m. p. (after washing with warm dilute sulphuric acid) 68—69°, raised slightly by admixture with diphenyl, m. p. 70°; (f) a residue, 2·5—3 g., having a diphenyl-like odour, b. p. above 250°.

Fractions (b) and (c) were united, washed with 4*N*-sulphuric acid, and dried over calcium chloride; the whole then distilled between 130° and 132° (chlorobenzene has b. p. 131—132°).

(2) *With dimethyl- and diethyl-chloroamines.* The Grignard solution (bromobenzene, 16 g.) reacted less vigorously with each of these chloroamines (9 c.c. and 12 c.c., respectively, in 100 c.c. of ether) than with 1-chloropiperidine. Chlorobenzene (3·5 g. and 5·2 g.) was isolated.

(3) *With chloramine-T.* There was no marked reaction between powdered chloramine-T (20 g., a trihydrate) and the Grignard solution (bromobenzene, 63 g.) at 0°, so the mixture was refluxed for 2½ hours. The ethereal layer afforded (a) benzene; (b) 12 g., b. p. 120—140°, refractionation of which gave chlorobenzene (8 g.), b. p. 130—132°; (c) a fraction, b. p. 200—250°, having the odour of thio-*p*-cresol, which was not examined; (d) much carbonised residue.

(4) *With dichloramine-T.* The reaction between dichloramine-T (28 g. in *ca.* 300 c.c. of ether) and the Grignard solution (bromobenzene, 20 g.; ether, 150 c.c.) was very violent, addition of each drop producing a hissing sound. Distillation of the ethereal solution gave chlorobenzene (about 0·5 c.c.), b. p. about 130°, but much charring and decomposition occurred and no other product was recognised.

(5) *With nitrogen trichloride.* Nitrogen trichloride in benzene solution (Hentschel, *Ber.*, 1897, **30**, 1792) did not react vigorously with a dilute ethereal solution of phenylmagnesium bromide (4

equivs.); the ethereal layer afforded only benzene and chlorobenzene, b. p. 130—131°.

(6) *With monochloramine.* The reaction was performed as described by Coleman and Hauser (*loc. cit.*), three times their quantities being used; about 8 g. of chlorobenzene were obtained from the ethereal layer.

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