The Reaction of Chloral with Cyclohexylmagnesium Bromide

By Vaughn W. Floutz

The action of chloral with various organomagnesium halides gives a number of reaction products depending principally upon the nature of the organomagnesium halide employed. Secondary alcohols which contain the trichloromethyl and alkyl groups have been prepared by several investigators.[1,2,3] In some instances the reported yields of such alcohols have been low,[2] and in one case[4] leading to the synthesis of trichloroisopropanol, trichloroethanol was formed in isolable quantity. A recent study[5] of the interaction of chloral and ethylmagnesium halides has shown that trichloroethanol is produced in yields up to 65%, but that no significant quantities of secondary alcohol are formed. Secondary alcohols containing the trichloromethyl group together with an aryl group are formed readily in good yield by the Grignard reaction.[6,7] Unpublished research by the author has shown that trichloromethylphenylcarbinol and trichloromethyl-*o*-tolylcarbinol can be prepared in yields as high as 70%. With the exception of trichloromethylbenzylcarbinol described first by Howard,[2] and more recently by Gilman and Abbott,[5] attempts to prepare secondary alcohols from chloral and phenyl substituted alkylmagnesium halides have proved unsuccessful. In this connection Dean and Wolf[8] have shown that β-phenylethylmagnesium bromide, γ-phenylpropylmagnesium bromide, and δ-phenylbutylmagnesium bromide react with chloral to give trichloroethanol, styrene and its homologs, and 1,4-diphenylbutane and its homologs, but no detectable secondary alcohol.

The object of this study was to investigate the behavior of cyclohexylmagnesium bromide with chloral.

Procedure.—The Grignard reagent was prepared by adding a 0.2-mole portion of cyclohexyl bromide dissolved in a like volume of anhydrous ether to 0.2 g.-atom of magnesium turnings in 200 ml. of anhydrous ether under an atmosphere of nitrogen. In the normal addition, 0.2 mole of freshly distilled chloral dissolved in a like volume of anhydrous ether was added slowly to the Grignard reagent and the mixture finally refluxed for one-half hour. In the inverse addition the Grignard reagent was removed and slowly added to 0.2 mole of freshly distilled chloral dissolved in 75 ml. of anhydrous ether. In both types of addition very little solid separated in the course of the reaction. The reaction mixture was treated with 1 *N* hydrochloric acid and the ether layer was separated and washed in turn with sodium bicarbonate solution, sodium bisulfite solution, and water, then dried over anhydrous sodium sulfate.

The dried ether was removed by distillation and the residue was heated in an oil-bath to a bath temperature of 110°. This gave a distillate which was found to be principally cyclohexene. The hydrocarbon was identified by its conversion to 1,2-dibromocyclohexane, boiling point 116–118° at 29 mm. In determinations carried out subsequent to the identification of cyclohexene, it was found advisable to add the cyclohexene distillate to the ether first removed by distillation, and treat the resulting ether solution with a slight excess of bromine. Following this the ether solution was washed with sodium bicarbonate solution and water. The dried ether was removed by distillation and the residue subjected to fractional distillation under diminished pressure to obtain the 1,2-dibromocyclohexane.

The residue from the removal of the cyclohexene was fractionated under diminished pressure. The first fraction collected gave upon redistillation an oily liquid distilling at 66–69° at 25 mm. This product was identified as trichloroethanol through the preparation of the *m*-nitrobenzoate, melting point 75°, and the α-naphthyl urethan, melting point 119°. Dicyclohexyl, boiling point 122–125° at 20 mm., was isolated from a higher boiling fraction.

From a number of determinations the average yields of trichloroethanol, 1,2-dibromocyclohexane, and dicyclohexyl were, where normal addition was followed, 12.5 g., 14.5 g. and 1 g.; where inverse addition was followed, 15.5 g., 21 g. and 2 g., respectively.

This investigation shows that the interaction of cyclohexylmagnesium bromide and chloral produces no secondary alcohol. Cyclohexene, trichloroethanol, and dicyclohexyl are formed in the reaction. Inverse addition gives in general better yields, but does not change the nature of the reaction products.

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[1] Henry, *Compt. rend.*, **138**, 205 (1904).

[2] Howard, This Journal, **48**, 774 (1926).

[3] Howard, *ibid.*, **49**, 1068 (1927).

[4] Kharasch, Kleiger, Martin and Mayo, *ibid.*, **63**, 2305 (1941).

[5] Gilman and Abbott, *J. Org. Chem.*, **8**, 224 (1943).

[6] Savarian, *Compt. rend.*, **146**, 297 (1908).

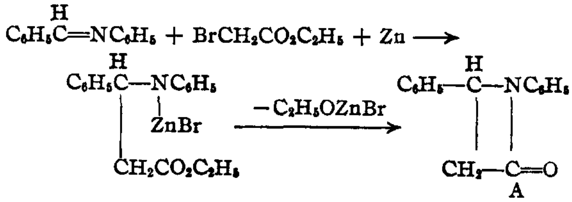
[7] Fritzman, *J. Russ. Phys.-Chem. Soc.*, **7**, 1046–1048 (1906).

[8] Dean and Wolf, This Journal, **58**, 332 (1936).

The Reformatsky Reaction with Benzalaniline

By Henry Gilman and Merrill Speeter

There appears to be no report on a Reformatsky reaction with an anil linkage.[1] We have observed that a mixture of ethyl bromoacetate and zinc adds to the anil linkage of benzalaniline to give a 56% yield of the β-lactam of β-anilino-β-phenylpropionic acid [A]



$$C_6H_5\overset{H}{C}{=}NC_6H_5 + BrCH_2CO_2C_2H_5 + Zn \longrightarrow C_6H_5\overset{H}{C}(CH_2CO_2C_2H_5){-}N(ZnBr)C_6H_5 \xrightarrow{-C_2H_5OZnBr} C_6H_5{-}\overset{H}{C}{-}NC_6H_5 \;(CH_2{-}C{=}O) \quad A$$

The structure of the lactam was established by the method of mixed melting points with a sample prepared by adding ketene to benzalaniline.[2]

Hydrolysis of the reaction mixture apparently is unnecessary to obtain the lactam. This indicates that the intermediately formed zinc complex can lose C_2H_5OZnBr (when ethyl bromoacetate is used) to cyclicize to the lactam.

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[1] See the excellent recent survey of the Reformatsky reaction by Shriner in Adams, "Organic Reactions," John Wiley and Sons, New York, N. Y., 1942, Vol. I, pp. 1–37.

[2] Staudinger, *Ber.*, **50**, 1037 (1917).