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

The Coupling Action of the Grignard Reagent. IV. Benzal Chloride and Benzotrichloride

BY REYNOLD C. FUSON AND WM. E. ROSS

It has been shown previously that the benzyl halides when treated with methylmagnesium iodide are converted into dibenzyl according to the equation: $2C_6H_5CH_2X + 2CH_3MgI = CH_3CH_3 + C_6H_5CH_2CH_2C_6H_5 + 2MgIX$.[1] This type of reaction has been reported by several investigators and appears to be applicable to a rather wide variety of types of halogen compounds. An examination of these various compounds, however, reveals the striking fact that the most conspicuous examples contain the skeletal grouping, $\mathrm{Ar{-}\overset{|}{\underset{|}{C}}{-}X}$, characteristic of arylmethyl halides. Thus, for example, the methoxybenzyl halides,[2] di-α-naphthylmethylchloromethane,[3] diphenylbromoethane,[2] ethylphenylbromomethane,[2] α-chlorophenylacetic acid[4] and the cyanobenzyl halides[5] give the coupling reaction and all of them possess the structural grouping in question.

On the other hand, benzal chloride and benzotrichloride—compounds which contain this structural unit—have not been found to undergo coupling. Reychler[6] examined the behavior of these two compounds toward phenylmagnesium bromide. In the case of benzotrichloride, he was unable to isolate any definite products. Benzal chloride gave a large amount of triphenylmethane and a small quantity of *s*-tetraphenylethane. Reychler attributed the formation of the latter to the action of metallic magnesium on diphenylchloromethane formed as an intermediate. In the light of Späth's work on diphenylbromomethane, we would now explain Reychler's result as due to the coupling of diphenylchloromethane by the action of the Grignard reagent.

In view of the fact, already pointed out, that benzal chloride and benzotrichloride possess the structural grouping which seems to be most effective in promoting the coupling tendency, the behavior of these two compounds toward the Grignard reagent has been reëxamined. The present paper is a report of this investigation.

Benzal Chloride.—In the case of benzal chloride methylmagnesium iodide was chosen as the reagent because of the high yields of coupling products which this reagent was found to give when used with the benzyl halides and with the cyanobenzyl halides. The results obtained were altogether unlike those reported by Reychler for phenylmagnesium

---

(1) Fuson, THIS JOURNAL, **48**, 2937 (1926).

(2) Späth, *Monatsh.*, **34**, 1965 (1913).

(3) Schmidlin and Massini, *Ber.*, **42**, 2384 (1909).

(4) MacKenzie, Drew and Martin, *J. Chem. Soc.*, **107**, 26 (1915).

(5) Fuson, THIS JOURNAL, **48**, 830 (1926).

(6) Reychler, *Bull. soc. chim.*, **35**, 737 (1906).

bromide and benzal chloride. It was found that methylmagnesium iodide effected direct coupling just as it did in the case of benzyl chloride, the second chlorine atom apparently having no influence upon the course of the reaction. The product was α-stilbene dichloride and the equation representing the reaction is

$$2C_6H_5CHCl_2 + 2CH_3MgI \longrightarrow C_6H_5CHClCHClC_6H_5 + CH_3CH_3 + 2MgICl$$

No evidence was obtained of the formation of cumene or of *s*-dimethyldiphenylethane—the products which would have been predicted in analogy with Reychler's results.[7] In view of this fact the reaction between benzal chloride and phenylmagnesium bromide has been reëxamined. As in Reychler's work, triphenylmethane was obtained, but no *s*-tetraphenylethane was isolated. Instead, considerable amounts of diphenyl and α-stilbene dichloride were found. These products evidently arise from the following reaction—a typical example of coupling

$$2C_6H_5CHCl_2 + 2C_6H_5MgBr = C_6H_5CHClCHClC_6H_5 + C_6H_5-C_6H_5 + 2MgBrCl$$

Benzotrichloride.—The Grignard reagent used in connection with the study of benzotrichloride was methylmagnesium chloride. Experiments were carried out with dilute solutions (0.2 molal) and with concentrated solutions (2 molal). In the presence of the dilute reagent benzotrichloride underwent coupling to yield tolane tetrachloride as shown by the equation

$$2C_6H_5CCl_3 + 2CH_3MgCl = C_6H_5CCl_2CCl_2C_6H_5 + CH_3CH_3 + 2MgCl_2$$

The reaction between benzotrichloride and the concentrated solution of methylmagnesium chloride gave an entirely different result. No tolane tetrachloride was isolated and instead there was obtained a mixture of the *cis* and *trans* forms of tolane dichlorides. The total yield of these isomers was about 22% of the theoretical; the proportion of the *trans* form to the *cis* was approximately 5 to 1.

It seemed probable that the effect of the concentration of the reagent was due not to a difference in the initial coupling reaction but to a difference in the stability of the initial product, tolane tetrachloride, toward the two solutions of the reagent. If this surmise were correct the tetrachloro compound which was stable in the dilute solution of the reagent should be attacked by the concentrated solution. Experiment has verified this hypothesis. In the 2 molal solution of methylmagnesium chloride tolane tetrachloride was found to react to give a mixture of the two geometrically isomeric tolane dichlorides.

Experimental

The Reaction of Benzal Chloride with Methylmagnesium Iodide.—To an approximately 2 molal solution of methylmagnesium iodide (prepared from 60 g. of methyl io-

---

[7] Since this work was done experiments have been carried out with benzal chloride and methylmagnesium chloride with results which are somewhat more in accord with those of Reychler. Evidence is now available which indicates that the halogen involved in the Grignard reagent used has a profound influence on the course of the reaction. A report of this work will appear in the near future.

dide and 10 g. of magnesium) was added over a period of two hours with continuous stirring 25 g. of benzal chloride. The reaction was very vigorous and caused the ether solution to boil steadily throughout the time of reaction. The stirring was discontinued and the reaction mixture was then heated externally and the boiling was maintained for two hours longer. Following this, the mixture was decomposed with concentrated hydrochloric acid and ice.

The supernatant ether layer was then separated and washed with a solution of sodium thiosulfate to remove any free iodine, and the ether was then evaporated by drawing a stream of air over the surface of the solution. The semi-solid residue which remained was separated by means of a suction filter into a colorless crystalline solid and a brown viscous oil. The yield of the solid before recrystallization was 4.3 g.

After three recrystallizations from glacial acetic acid the solid was obtained in large, colorless prisms melting at 189–190°. A mixture of this compound with α-dichlorostilbene (melting point 190°)[8] melted at 190°.

The brown, viscous oil did not crystallize and could not be distilled even at 200° at 10 mm. No evidence was obtained of the presence of cumene.

The Reaction of Benzal Chloride with Phenylmagnesium Bromide.—A mixture of 150 cc. of a 1.6 molal solution of phenylmagnesium bromide and 32 g. of benzal chloride was heated under reflux. A crystalline precipitate began to separate almost immediately and at the end of three hours the liquid contained a large amount of suspended solid. Water and hydrochloric acid were added until two clear layers resulted. The ether layer was separated and the ether was removed on the steam-bath. The residue was a brown, lachrymatory oil which when cooled in an ice-bath deposited crystals melting at 190–192° after one recrystallization from glacial acetic acid. A mixture of these crystals with α-stilbene dichloride melted at 190–192°.

The remainder of the oily material was subjected to distillation. Ten grams of unchanged benzal chloride was recovered. A considerable amount of diphenyl was also removed during the distillation. The tarry residue deposited crystals which were filtered and recrystallized from ethyl alcohol. A mixed melting point determination showed this compound to be triphenylmethane (melting point 92°).

The Reaction of Benzotrichloride with Methylmagnesium Chloride in Dilute Solution.—To 500 cc. of an approximately 0.2 molal solution of methylmagnesium chloride in ether was added slowly 19.5 g. of benzotrichloride in 50 cc. of anhydrous ether. There was no evidence of a reaction. The mixture was then heated under reflux with continued stirring for three hours. Decomposition of the reaction mixture with water and hydrochloric acid and subsequent distillation of the ether from the ether layer gave a brown oil. This material was placed in a 10% solution of sodium hydroxide and subjected to steam distillation. About 3 cc. of unchanged benzotrichloride was recovered in the distillate. A crystalline substance was left in the distilling flask. After six recrystallizations from glacial acetic acid this compound melted at 161–162°. One gram of the pure compound was obtained in the form of a fine, white powder. A mixture of this compound with an authentic specimen of tolane tetrachloride (melting point, 161–162°)[9] showed no depression in the melting point.

The Reaction of Benzotrichloride and Methylmagnesium Chloride in Concentrated Solution.—To 200 cc. of an approximately 2 molal solution of methylmagnesium chloride was slowly added[10] 39 g. of benzotrichloride. Although the addition was carried out in a dropwise manner it caused the ether to boil vigorously. After the addition was complete and the reaction had apparently ceased, the mixture was heated under

---

(8) Zincke, *Ber.*, **10**, 1002 (1877).

(9) Zinin, *Ann.*, **34**, 188 (1840).

(10) This as well as other solutions of methylmagnesium chloride used in these experiments was analyzed by titration with acid.

reflux for an hour. The mixture was decomposed in the manner described for the experiment which was carried out in dilute solution. Also, the steam distillation was conducted in the way described for the preceding experiment. However, the distillate in this case came over very slowly. In addition to a few cc. of oil the distillate contained a waxy solid which was collected over a period of eighteen hours of continued distillation. This material was a mixture of *cis* and *trans* tolane dichlorides. The two isomers were separated by fractional crystallization from alcohol. The *trans* isomer melted at 63° and the *cis* form at 138–139°. In several experiments there was obtained an average yield of 22% of that theoretically possible for the two dichlorides. The proportion of *cis* to *trans* was about 1 to 5.

Anal. Calcd. for $C_{14}H_{10}Cl_2$: C, 28.5. Found for the *cis* isomer: Cl, 28.5. Found for the *trans* isomer: Cl, 28.6.

The Reaction between Methylmagnesium Chloride and Tolane Tetrachloride.—Seven-tenths gram of tolane tetrachloride was heated under reflux for four hours with an excess of a 2 molal solution of methylmagnesium chloride. Decomposition of the reaction mixture in the usual manner gave a solid melting from 63 to 80° which proved to be a mixture of the isomeric tolane dichlorides. The yield was 0.2 g.

Summary

Methylmagnesium iodide has been shown to exert a coupling action on benzal chloride. The product, α-stilbene dichloride (C_6H_5CHCl-$CHClC_6H_5$), was likewise obtained when phenylmagnesium bromide was allowed to react with benzal chloride.

A similar coupling was observed with benzotrichloride. When treated with a dilute solution of methylmagnesium chloride it gave tolane tetrachloride ($C_6H_5CCl_2CCl_2C_6H_5$).

In concentrated solutions of methylmagnesium chloride benzotrichloride has been found to yield a mixture of the *cis* and *trans* forms of tolane dichloride ($C_6H_5CCl{=}CClC_6H_5$).

The same mixture of isomers was obtained when tolane tetrachloride was treated with the concentrated solution of methylmagnesium chloride.

The latter result has been interpreted to mean that tolane tetrachloride is produced alike by dilute and by concentrated solutions of the reagent but that in the latter case it is subsequently transformed into the tolane dichlorides.

URBANA, ILLINOIS

RECEIVED JULY 18, 1932
PUBLISHED FEBRUARY 9, 1933