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CYANOGEN CHLORIDE WITH ORGANOMAGNESIUM COMPOUNDS

George H. Coleman and Robert W. Leeper

A Grignard reagent is commonly represented by the formula RMgX. It has been established, however, that the following equilibrium exists in such a reagent (1, 2, 3).

$$2RMgX \rightleftarrows R_2Mg + MgX_2$$

The assumption has been made that almost without exception the reactions of RMgX and R_2Mg are the same and that therefore the representation of the reagent as RMgX is permissible. One of the first exceptions noted was in the reaction between alkyl sulfonates and the Grignard reagent (4, 5, 6). In this work it was shown that each component in the above equilibrium has a different effect in the reaction.

$$RMgX + (CH_3)_2SO_4 \rightarrow CH_3X + CH_3OSO_2OMgR$$
$$R_2Mg + (CH_3)_2SO_4 \rightarrow RCH_3 + CH_3OSO_2OMgR$$
$$MgX_2 + 2(CH_3)_2SO_4 \rightarrow 2CH_3X + (CH_3OSO_2O)_2Mg$$

Recent work in this laboratory by Coleman and Blomquist (7) furnishes another example of a difference in the reactions of RMgX and R_2Mg. In the reaction of monochloroamine with Grignard reagents, two nitrogen containing products, ammonia and a primary amine, are obtained when the reaction mixture is hydrolyzed. The formation of these two products may be represented by the following equations:

$$RMgX + NH_2Cl \rightarrow RNH_2 + MgXCl$$
$$RMgX + NH_2Cl \rightarrow RCl_2 + MgX(NH_2)$$

Using the Grignard reagents prepared from n-butyl chloride, bromide, and iodide the average yields of n-butylamine were shown to be 57 percent, 29 percent and 12 percent respectively. In the reactions of monochloramine with pure di-n-butylmagnesium the yields of n-butylamine were much higher being between 82 percent and 97 percent.

The present work with cyanogen chloride was undertaken to determine whether this compound did not also show a difference in its reactions with the substances present in a Grignard reagent.

One of the earliest recorded reactions of cyanogen chloride with an organometallic compound was reported by Gal (8) in 1868, when he obtained a nitrile by the action of zinc ethyl on cyanogen chloride. Ciamician and Dennstedt (9) obtained cyanopyrrole from potassium pyrrole and cyanogen chloride. Others who have reported work in this field are Blaise (10), Ostrogovich (11), and Grignard (12).

In the present work the reactions of cyanogen chloride with di-n-butylmagnesium and the Grignard reagent prepared from n-butyl bromide, were studied. These organometallic compounds were selected as representative of the aliphatic class and also because they had been used in the previous work of Coleman and Blomquist. n-Butyl bromide was used rather than n-butyl chloride since the chloride is one of the products of the reaction studied. Obviously n-butyl iodide might have been used but with monochloroamine the yields of primary amines had been found to be much better with reagents prepared from bromides than from iodides.

The experimental results of this work have shown that there is a distinct difference between the relative percentage yields of the nitrile and chloride obtained with di-n-butylmagnesium and the Grignard reagent prepared from n-butyl bromide. The reactions occurring with these reagents may be represented by the following equations. In these equations, no attempt is made to indicate any possible intermediate compounds.

$$RMgX + ClCN \rightarrow RCN + MgXCl$$
$$RMgX + ClCN \rightarrow RCl + MgX(CN)$$
$$R_2Mg + ClCN \rightarrow RCN + RMgCl$$
$$R_2Mg + ClCN \rightarrow RCl + RMgCN$$

By reference to Table I, in which the results from several runs with the two reagents are given, it may be observed that with the Grignard reagent prepared from n-butyl bromide, the average yield of valeronitrile was about 47 percent and that of n-butyl chloride about 37 percent. With di-n-butylmagnesium, the average percentage yields of the nitrile and chloride were 34 percent and 48 percent respectively. In all reactions a slight excess of cyanogen chloride was used since there was the possibility of a reaction between any valeronitrile and an excess of organomagnesium compound. It is quite possible that it might have been permissible to use an excess of the organomagnesium compound since Grignard (13) found it necessary to heat the reaction mixture to 180-90°C. in order to form the ketone, presumably by further reaction of the nitrile.

Table I. Yields of n-Valeronitrile and n-Butyl Chloride

Type Reagent	Moles Org. Mg. Compound	Moles ClCN	Moles RCN	Moles RCl	Percentage Yield RCN	Percentage Yield RCl
RMgX	0.322	0.322	0.150		46.6	
RMgX	0.326	0.325	0.145		44.8	
RMgX	0.308	0.328	0.149	0.113	48.4	36.6
RMgX	0.267	0.290	0.125	0.099	47.2	37.2
R_2Mg	0.202	0.433	0.138		34.2	
R_2Mg	0.188	0.390	0.127	0.181	33.9	48.1
R_2Mg	0.134	0.293	0.091	0.128	34.1	47.9
R_2Mg	0.182	0.480		0.184		50.5

EXPERIMENTAL

Cyanogen Chloride. — This compound was prepared by a modification of the Jennings and Scott (14) and Dieterle (15) methods. Powdered sodium cyanide was suspended in carbon tetrachloride, a very little glacial acetic acid added and dry chlorine passed into the mixture at such a rate that there was no excess chlorine passing through the apparatus. The temperature was maintained at about —5°. The time required for completing reactions in which 20 g. of sodium cyanide was used was about three hours.

The cyanogen chloride was distilled into a suitable receiver, a few grams of mercury added, the mixture refluxed to remove chlorine and the product finally distilled. The yield was 75-80 percent of a pure product which did not contain free chlorine.

The method of analysis of the cyanogen chloride was essentially that described by Mauguin and Simon (16).

Grignard Reagent. — The Grignard reagent was prepared in the usual way from n-butyl bromide in anhydrous ether solution. It was analyzed by the acid titration method of Gilman and coworkers (17).

Di-n-butylmagnesium. — The solution of di-n-butylmagnesium was prepared by the method described by Coleman and Blomquist (7).

Reaction of the Grignard Reagent with Cyanogen Chloride. — About 0.3 mole of cyanogen chloride, which represented a slight excess for the amount of Grignard reagent to be added was dissolved in about 300 ml. of anhydrous ether and cooled by surrounding the reaction flask with a bath of ice and salt. To this was added dropwise a cooled solution of the Grignard reagent in about 150 ml. of anhydrous ether. When the addition was completed, the mixture was refluxed over a hot plate for fifteen minutes. A precipitate appeared, ranging in color from light brown to brownish-red. The mixture was cooled and hydrolized with ammonium chloride solution. The two layers were separated and the water layer extracted twice with ether. The combined ether solution was shaken for ten minutes with a fairly concentrated solution of sodium hydroxide to remove the excess cyanogen chloride. The ether layer was separated and dried over calcium chloride.

Reaction of Di-n-butylmagnesium with Cyanogen Chloride.—This reaction was carried out in much the same manner as that with the Grignard reagent. Special care was necessary, however, to keep this solution under an atmosphere of nitrogen at all times because it is spontaneously inflammable with oxygen.

Fractionation of Reaction Mixtures.—The dry ethereal solution containing n-valeronitrile and n-butyl chloride was carefully fractionated using a modified Widmer column. The effectiveness of the column was first determined by separating known mixtures of these compounds. In the reaction mixtures from Grignard reagents there was always a little n-butyl bromide. The distillation of the relatively high boiling valeronitrile was carried out under reduced pressure. The purity of the final fractions was determined by both the boiling point and the index of refraction.

In the case of products resulting from the reaction with *di-n*-butylmagnesium in which there could be no n-butyl bromide the amount of n-butyl chloride present in the ethereal solution before fractionation was determined by analysis of a small sample of the solution for chloride. A slightly modified peroxide bomb method of analysis was used. The analytical results were in close agreement with the results obtained by distillation. In Table 1 are given the results of several typical runs with Grignard reagents and with solutions of di-n-butylmagnesium.

SUMMARY

(1) The reactions of cyanogen chloride with n-butylmagnesium bromide and di-n-butylmagnesium have been studied.

(2) With di-n-butylmagnesium the percentage yield of valeronitrile is less and the percentage yield of n-butyl chloride greater than in the reaction of cyanogen chloride with n-butylmagnesium bromide.

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