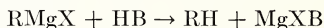


Action of Ammonia on Hexynyl Magnesium Halides

G. F. HENNION and G. M. WOLF,
University of Notre Dame

It is a well known fact that "acidic" substances decompose Grignard reagents as follows,



where HB represents water, alcohols, ammonia, primary and secondary amines, etc.

However, the acetylenic Grignard reagents, $\text{RC}\equiv\text{CMgX}$, are related to the acetylides, and acetylides of first and second group metals are stable to ammonia. It was, therefore, thought of some interest to study the action of ammonia on typical acetylenic Grignard reagents. Hexynyl magnesium chloride and bromide were selected for this work. It was thought that ammonia might favor the following transformation,



rather than ammonolysis. This anticipation was not realized, and ammonia, either liquid or gaseous, was found to decompose the hexynyl magnesium halides, though incompletely. Treatment of ethereal solutions of the hexynyl magnesium halides with ammonia yielded bulky, amorphous, white precipitates. These were filtered, dried, weighed, and analyzed for magnesium, halogen, and ammonia nitrogen. In each instance these data correspond roughly to compositions in accord with the formula,



The reactions affording such precipitates must be complex. A suggested equation, in accord with experimental observations, is:

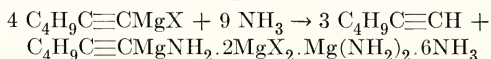


Table I presents the experimental data upon which these conclusions are based.

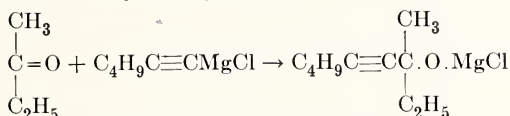
TABLE I.—Experimental Data: Action of Ammonia on Hexynyl Magnesium Halides.

(a) Experiments with $\text{C}_4\text{H}_9\text{C}\equiv\text{CMgCl}$									
Precipitate calculated for $\text{C}_4\text{H}_9\text{C}\equiv\text{CMgNH}_2 \cdot 2\text{MgCl}_2 \cdot \text{Mg}(\text{NH}_2)_2 \cdot 6\text{NH}_3$									
Amount $\text{RC}\equiv\text{CMgCl}$ Mols	NH_3 added as	Analyses of Precipitate							
		Wt. Ppt., g.		Calc. (%)			Found (%)		
		Calc.	Found	Mg	Cl	N	Mg	Cl	N
0.5	gas	58.81	61.9	20.68	30.15	26.80	21.81	30.87	27.70
0.5	liqd.	58.81	62.5	20.68	30.15	26.80	16.95	29.00	26.46

(b) Experiments with $C_4H_9C\equiv CMgBr$
 Precipitate calculated for $C_4H_9C\equiv CMgNH_2 \cdot 2MgBr_2 \cdot Mg(NH_2)_2 \cdot 6NH_3$

Amount $RC\equiv CMgBr$ Mols	NH_3 added as	Analyses of Precipitate							
		Wt. Ppt., g.		Calc. (%)			Found (%)		
		Calc.	Found	Mg	Br	N	Mg	Br	N
0.5	gas	81.04	86.1	15.01	49.31	19.45	14.09	48.90	19.17
0.5	liqd.	81.04	88.7	15.01	49.31	19.45	14.13	51.09	19.25

That ammonia causes incomplete ammonolysis is shown also by other facts. For example, addition of methyl ethyl ketone, *after ammonia*, gave a 14.3% yield of 3-methyl-4-nonyne-3-ol:



In a similar manner, butyl bromide gave an 8% yield of 5-decyne and diethyl sulfate gave a 6.4% yield of 3-octyne. These reactions indicate clearly that the ammonia had decomposed the Grignard reagent incompletely.

Experimental

Materials.—Butyl acetylene was obtained by a modified Picon synthesis¹. Dry magnesium turnings and ether distilled from phosphorus pentoxide were used in every case.

Action of Liquid Ammonia on Hexynyl Magnesium Chloride.—To one-half mole (12.16 gm.) of magnesium turnings covered with dry ether in a three-liter three-necked flask, equipped with a mercury stirrer and a reflux condenser, was added ethyl chloride through a dropping funnel. The flask was cooled in a water bath, and the stirring was continued during the addition of the ethyl chloride.

Then one-half mole (41.0 gm.) of butyl acetylene in an equal volume of dry ether was added drop-wise to the ether solution of ethyl magnesium chloride. After all the butyl acetylene had been added, the ether solution was refluxed until all the ethane and unreacted ethyl chloride were driven off. After replacing the condenser with a long piece of glass tubing, used as a vent, the flask was cooled in a bath of carbice and acetone. Then 1.5 liters of liquid ammonia was slowly introduced to the reaction flask through the dropping funnel. The addition of liquid ammonia caused a milky-white precipitate to form which had a tendency to cake on the side of the flask unless vigorous stirring was employed.

Stirring was continued for a half hour; then the entire mixture was filtered through a large funnel. The process of filtration required

¹ Vaughn, Hennion, Vogt, and Nieuwland, 1937. Journ. Org. Chem. 2, 1. Hennion, 1938. Proc. Indiana Acad. Sci., 47, 116.

from three to four hours, and even after that time the precipitate was still very pasty. After the liquid ammonia evaporated from the filtrate, the remaining liquid was distilled, and 18.5 gm. of butyl acetylene was recovered.

The precipitate, a pasty white mass, was dried over concentrated sulfuric acid in a vacuum desiccator. Since the acid absorbed so much ammonia, it was necessary to change the acid at least three times before the precipitate reached a constant weight. The final product was a fine, white, flaky powder which obtained a constant weight after one week's drying. This white powder was analyzed for magnesium, chlorine, and nitrogen.

Action of Gaseous Ammonia on Hexynyl Magnesium Chloride.—

One-half mole (70.46 gm.) of hexynyl magnesium chloride was prepared in the same manner as described above. At this point the dropping funnel was replaced by a piece of glass tubing extending just above the surface of the liquid. With continual stirring gaseous ammonia was introduced into the reaction flask until no more precipitate was formed. After adding 200 cc. of dry ether the resulting mixture was filtered and treated as described above.

Action of Liquid Ammonia on Hexynyl Magnesium Bromide.—

One-half mole (92.68 gm.) of hexynyl magnesium bromide was prepared and treated with liquid ammonia in the same manner as described for the treatment of hexynyl magnesium chloride with liquid ammonia except, of course, that ethyl bromide was used as the starting reagent in place of ethyl chloride.

Action of Gaseous Ammonia on Hexynyl Magnesium Bromide.—

This experiment was carried out in a manner similar to that described under the action of gaseous ammonia on hexynyl magnesium chloride. After analyzing this precipitate for magnesium, bromine, and nitrogen, 80 gm. was placed in a two-liter round bottom flask equipped with a reflux condenser. After adding 500 cc. of anhydrous benzene, the mixture was refluxed for one hour in order to extract any free organic matter that might be present in the precipitate. After the mixture was filtered, distillation of the benzene filtrate revealed no dissolved organic matter.

Preparation of 3-methyl-4-nonyne-3-ol.—One-half mole (70.46 gm.) of hexynyl magnesium chloride was prepared by the method described above. After the addition of 1.5 liters of liquid ammonia, the stirring was continued for a short time so as to insure good suspension of the insoluble precipitate. Then one-half mole (36.06 gm.) of methyl ethyl ketone was added slowly to the reaction mixture through the dropping funnel. Stirring was continued until nearly all the liquid ammonia evaporated; then more dry ether was poured into the flask.

The mixture was hydrolyzed with 500 cc. of 10% hydrochloric acid solution. The ether layer was separated, washed with water several times, and then washed with 200 cc. of 20% sodium carbonate solution, washed again with water, and the ether portion dried over anhydrous

magnesium sulfate. Upon distillation a 14.30% yield of the condensation product, 3-methyl-4-nonyne-3-ol, was obtained.

Preparation of 5-decyne.—A similar procedure was followed for preparing 5-decyne as for the synthesis of 3-methyl-4-nonyne-3-ol, except that one-half mole (68.5 gm.) of butyl bromide was added to the reaction mixture in place of the methyl ethyl ketone. A 7.95% yield of 5-decyne was obtained.

Preparation of 3-octyne.—In preparing 3-octyne the same procedure was followed as given above, except one mole (154.14 gm.) of diethyl sulfate was used, according to the mechanism proposed by Thorn, Hennion, and Nieuwland². A 6.35% yield of 3-octyne was obtained.

Summary

Ammonia has been found to decompose hexynyl magnesium halides incompletely. The products of such reactions are complex amorphous precipitates, insoluble in ether and in liquid ammonia. Hypothetical formulas have been ascribed to these materials: $C_6H_9-C\equiv MgNH_2 \cdot 2MgX_2 \cdot Mg(NH_2)_2 \cdot 6NH_3$, where X represents Cl or Br.

² Thorn, Hennion, and Nieuwland, 1936. Journ. Am. Chem. Soc., 58, 796.