Hydrolysis of Heptamethyl-β-methyl Lactoside.—The heptamethyl-β-methyl lactoside (0.95 g.) was dissolved in 1 *N* sulfuric acid (5 ml.) and the solution was heated on the boiling water-bath for 2.5 hours. The hydrolysate was diluted with water to 75 ml., neutralized with barium carbonate and filtered. The filtrate was evaporated *in vacuo* (bath temp., 50–60°) to yield a sirupy mixture of 2,3,6-trimethyl-D-glucose and 2,3,4,6-tetramethyl-D-galactose which was separated into its constituents by means of partition chromatography on a column of cellulose[7] using methyl ethyl ketone–water azeotrope as the partitioning solvent,[13] and an automatic fractionating device.[7]

The 2,3,6-trimethyl-D-glucose so obtained as the slower moving component showed m.p. and mixed m.p. 115–117°[14] after recrystallization from benzene–petroleum ether and once from benzene.

The 2,3,4,6-tetramethyl-D-galactose, the faster moving component to emerge from the column was distilled (b.p. (bath temp.) 160°, 0.5 mm.) and converted directly to the anilide; m.p. and mixed m.p. 196–197° (after recrystallization from ethyl acetate).[15]

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

Studies of Non-aqueous Solvates. VI. The Preparation of Magnesium Amide Bromide

BY H. H. ROWLEY AND LEONARD N. DEVONSHIRE

The ammonolysis of ethylmagnesium bromide has been carried out in solutions of ethyl ether or benzene saturated with ammonia. The slightly soluble product obtained has been identified as magnesium amide bromide, $Mg(NH_2)Br$, rather than the possible imido or nitrilo ammonobasic salt. The existence of two ammoniates of magnesium amide bromide has been indicated. The diammoniate is apparently formed at room temperatures when excess ammonia is present, the monoammoniate resulting from partial desolvation of the diammoniate. The diammoniate of magnesium amide bromide has been found to be relatively stable under dry atmospheric conditions, but may be changed to the monoammoniate by gentle heating at lower pressures. The decomposition to the completely desolvated magnesium amide bromide requires heating at higher temperatures and preferably reduced pressure. The desolvated product has been found to be stable to over 200°. An attempt to prepare ethyl etherates of magnesium amide bromide was not successful.

The existence of ammonobasic salts of the magnesium halides has been previously reported but no study has been made of their preparation or properties. Meunier,[1] Oddo and Calderaro,[2] Cornell,[3] Pickard[4] and others have reported the formation of ammonobasic salts when various Grignard reagents and addition compounds of the Grignard reagent were decomposed with ammonia. Usually, the apparently inorganic precipitates were not extensively analyzed or investigated.

As a continuation of a study of non-aqueous solvates of magnesium bromide and related compounds,[5a–g] it was decided to investigate the precipitates obtained by the ammonolysis of Grignard reagents. Preliminary work indicated that the precipitates obtained in ketimine formation[4] were not of sufficient purity to be used in the investigation. It was therefore decided to undertake the preparation of pure magnesium amide bromide and to study some of its properties.

Experimental

The experimental procedure in general involved the preparation of ethylmagnesium bromide followed by the ammonolysis of the Grignard reagent. The product was obtained as a fine white precipitate which was separated from the liquid medium. This product was analyzed, and some reactions such as desolvation and reaction with other solvents were studied.

Preparation and Ammonolysis of the Grignard Reagent.—A filtered solution of the ethylmagnesium bromide was prepared from 25 ml. of pure ethyl bromide, 15 g. of magnesium turnings and 150 ml. of ethyl ether. Preliminary work indicated a much better product could be obtained by the slow addition of the Grignard reagent to a relatively inert solvent such as benzene or ethyl ether saturated with ammonia. Mechanical stirring during the addition was also found advisable.

Anhydrous ammonia was introduced into the reaction flask containing 200 ml. of benzene or ethyl ether by means of a gas inlet tube which extended well below the surface of the inert liquid. A slow stream of nitrogen was also passed over the reaction mixture. A gas outlet tube allowed the escape of excess ammonia, nitrogen and ethane formed during the ammonolysis of the Grignard reagent. The product was obtained as a fine white suspension. When ether was used as an inert solvent, it was necessary to add additional ether during the reaction to keep the mixture from becoming too thick. With benzene, the loss of solvent was less noticeable.

Isolation of Product.—The product, suspended in the inert solvent, was transferred from the reaction flask by filtering through a sintered glass filter in an anhydrous nitrogen atmosphere. The cake formed by gentle suction was then easily broken up with a spatula and dried to a fine powder.

Since all of the solvent was not removed by the filtration procedure, and since experimental results indicated the possibility that rather stable ammoniates were formed, it was found necessary to heat the original product to obtain the desolvated product. The most satisfactory procedure was to use low pressures during the heating. The original filtered product was placed in a flask, connected to an oil-pump vacuum, and evacuated 5–10 minutes until most of the excess solvent had evaporated. The flask was then immersed in a hot wax-bath kept at 180°. After 4 hours the original sample was completely desolvated. An additional 10 hours evacuation at 180° showed no appreciable change in composition. The product was a fine, faintly gray powder.

Several other methods were tried including extraction of ammonia from the solid suspended in benzene using anhydrous calcium chloride. Desolvation was also attempted by heating at atmospheric pressure in a stream of dry nitrogen. The latter method was also slow since too rapid heating sometimes resulted in partial fusion of the solid.

Analysis.—Early experience showed that the products being analyzed liberated ammonia at a rapid rate when treated with water or absolute ethanol and that some am-

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(1) L. Meunier, *Compt. rend.*, **136**, 758 (1903).

(2) C. Oddo and E. Calderaro, *Gazz. Chim. Ital.*, **53**, 94 (1923).

(3) E. F. Cornell, THIS JOURNAL, **50**, 3314 (1928).

(4) P. L. Pickard and D. J. Vaughan, *ibid.*, **72**, 5017 (1950).

(5) H. H. Rowley, (a) *ibid.*, **72**, 3305 (1950); (b) *ibid.*, **63**, 1908 (1941); (c) *Proc. Iowa Acad. Science*, **47**, 159 (1940); (d) THIS JOURNAL, **61**, 1949 (1939); (e) *ibid.*, **59**, 631 (1937); (f) *ibid.*, **58**, 1337 (1936); (g) *ibid.*, **52**, 3523 (1930).

TABLE I

ANALYTICAL RESULTS

Prep. No.	Treatment	Weight %			Atom ratio		
		Mg	N	Br	Mg	N	Br
12-1	C_6H_6 ammonolysis; aspirator vacuum 1 hr. 80°		24.3	52.1		2.7	1
12-2	Suspended in anhy. Et_2O 48 hr., dried atm. conditions		17.0	36.4		2.7	1
13-3	C_6H_6 ammonolysis; OPV[a] 24 hr. 140°	19.5	11.8	63.8	1.0	1.0	1
13-5	Residue 13-3 in C_6H_6, NH_3 for 30 min.		20.6	34.6		3.4	1
16-3	Et_2O ammonolysis; NH_3 in excess		17.0	31.2		3.1	1
16-4	Residue 16-3, OPV 36 hr. at room temp.		22.0	48.9		2.8	1
27-7	Et_2O ammonolysis: OPV 16 hr. 130°		14.4	63.6		1.3	1
27-8	Residue 27-7 in Et_2O, NH_3 for 30 min.		13.3	21.5		3.5	1
27-10	OPV 10 hrs. 143°		12.3	64.5		1.1	1
32-1	Et_2O ammonolysis; dried atm. conditions		15.1	24.1		3.5	1
32-2	OPV 4 hr. 180°		11.6	62.1		1.0	1
32-4	OPV 14 hr. 180°	18.9	10.1	63.0	1.0	0.92	1
34-1	C_6H_6 ammonolysis; dried atm. conditions					3.4	1
34-2	OPV 4 hr. 186°	18.8	10.7	63.7	1.0	1.0	1
Theoretical:	$MgNH_2Br$	20.2	11.6	66.4	1	1	1
	$MgNH_2Br.NH_3$	17.7	20.4	58.2	1	2	1
	$MgNH_2Br.2NH_3$	15.8	32.4	51.8	1	3	1

[a] Oil pump vacuum.

monia was lost by attempting to dissolve the sample in an open container. To avoid this loss of ammonia 3–5 g. of the weighed sample was placed in an erlenmeyer flask fitted with a dropping funnel. About 75 ml. of water was placed in the funnel and allowed to enter the flask slowly. Before all the water had been added, 100 ml. of sulfuric acid, diluted 1:4 was placed in the funnel and run into the sample. The contents of the flask were then transferred quantitatively and diluted in a 250-ml. volumetric flask. Aliquot portions were used for analyses of bromine, nitrogen and magnesium by standard procedures.

Analyses of the completely desolvated product indicated a purity of 92–99% calculated as magnesium amide bromide and a yield of over 90% based on the ethyl bromide used. The slight darkening of the product on prolonged heating at higher temperatures indicated the presence of a small amount of organic impurity.

Reaction with Solvents.—Attempts were made to find a solvent from which the product might be recrystallized. Among the solvents tried were ethyl ether, 1,4-dioxane, carbon tetrachloride, chloroform, benzene, pyridine and dimethylformamide. None of these solvents appeared to react with or dissolve more than a trace of either the desolvated product or the original product, believed to be ammoniated. Water, alcohols, aliphatic ketones and other compounds with active hydrogen could not be used because they reacted with the product to liberate ammonia.

Results

More than thirty-six preparations were made under varying conditions. A few pertinent analytical results are summarized in Table I. The last three columns have been calculated from experimental data and summarized for ready reference in interpreting these results. Magnesium analysis was not considered necessary for each sample because in every analysis made, bromine and magnesium were present in approximately the same ratio.

Theoretically, ammonia is capable of reacting with one, two or three molecules of a Grignard reagent to give ethane and magnesium amide bromide, $MgNH_2Br$, imidobismagnesium bromide, $NH(MgBr)_2$ or nitrilotrismagnesium bromide, $N(MgBr)_3$, respectively. Sudborough and Hibbert[6] have reported the imido-type of compound is formed at elevated temperatures when primary amines react with ethylmagnesium iodide. Further, Oddo and Calderaro[2] have shown that when ethylmagnesium iodide is decomposed with ammonia at lower temperatures, the evolution of ethane is quantitative for the formation of the magnesium amide iodide. Since, in the present work, ammonia was always present in excess during the ammonolysis, the formation of the imido- and nitrilo-types might be considered negligible.

Another indication that the amide salt was the principal compound formed during ammonolysis is shown by the analyses in Table I. If the imido- or nitrilo-compound were formed, in appreciable amounts, analysis would show atom ratios of nitrogen:bromine of less than unity, *e.g.*, $^1/_2$ to 1 for imidomagnesium bromide. Since ratios less than unity were never obtained on reliable preparations, it was concluded that the product obtained was primarily magnesium amide bromide, $MgNH_2Br$.

With the original filtered product, the ratio of nitrogen: bromine was always greater than unity. To obtain a 1:1 ratio it was necessary to heat the product, preferably at reduced pressure. To account for the higher ratios it is necessary to postulate the formation of ammoniates, in which a molecule of magnesium amide bromide has added one or more molecules of ammonia as ammonia of solvation.

Ratios of nitrogen:bromine greater than 3:1 were always obtained when excess ammonia had been passed through the suspension in benzene or ethyl ether (No. 13-5, 16-3, 27-8, 32-1, 34-1). Some of the excess nitrogen could be ammonia dissolved in the solvent which was always present after filtering the solid. However, oil pump vacuum on a sample at room temperature for 36 hours (No. 16-4) failed to lower the ratio appreciably, indicating approximately two moles of ammonia are rather firmly bound to the magnesium amide bromide. Further, a sample having a nitrogen:bromine ratio of 2.7:1 was shaken with ethyl ether for two days. Analyses Nos. 12-1 and 12-2 indicated no decrease in the nitrogen:bromine ratio. If the excess nitrogen were due to occluded ammonia, the ratio would be expected to decrease due to the solubility of ammonia in ether.

Whereas the nitrogen:bromine ratio could be lowered to less than 3:1 by evacuation at room temperature (No. 16-4) or by short heating at higher temperatures (No. 12-1), a longer period of time or higher temperature was required to bring the ratio below 2:1. To lower the ratio to 1:1 required much longer periods of time or still higher temperatures (No. 13-3, 27-10, 32-2, 34-2). However, once the ratio reached 1:1 the compound appeared to be stable to at least 200° (No. 32-4). This would indicate that one nitrogen is present as the amido-group and that the other two (or possibly more) are bound rather firmly but can be displaced by heating below 200°. These are apparently not liberated with equal ease. It is postulated that they might well be the diammoniate, $MgNH_2Br\cdot 2NH_3$, and monoammoniate, $MgNH_2Br\cdot NH_3$, of the magnesium amide bromide.

Meunier[1] and Oddo and Calderaro[2] have reported solid etherates of magnesium amide iodide. Attempts to obtain solid etherates of magnesium amide bromide by ammonolysis in ethyl ether solution or by placing the deammoniated product in prolonged contact with ether were unsuccessful. Since the desolvation process might have rendered the product inactive with respect to solvating properties, samples of the desolvated product were suspended in benzene or ether and ammonia passed through the mixture for 30 minutes. Analysis of the residue (No. 13-5, 27-8) showed the ammoniated product was readily re-formed.

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(6) J. Sudborough and N. Hibbert, *J. Chem. Soc.*, **95**, 477 (1909).