1. Sjöquist, J. *Acta Chem. Scand.* **7** (1953) 447.
2. Haines, W. and Drake, N. *Federation Proc.* **9** (1950) 180.
3. Wallenfels, K. and Christian, W. *Angew. Chem.* **65** (1953) 459.
4. Sjöquist, J. *Biochim. et Biophys. Acta* **16** (1955) 283, and unpublished.
5. Edman, P. *Acta Chem. Scand.* **4** (1950) 277.
6. Ingram, V. M. *J. Chem. Soc.* **1953** 3717.
7. Edman, P. and Lauber, K. *Acta Chem. Scand.* **10** (1956) 466.

Received October 26, 1956.

Isotope Effect in the Hydrolysis of Grignard Compounds. II *

LARS OLOF ASSARSSON

Nobel Institute of Chemistry, Stockholm 50, Sweden

Measurements of the hydrogen isotope effect in the hydrolysis of methylmagnesium iodide and phenylmagnesium iodide in a solution of anisole and pyridine were reported in a previous preliminary paper¹. Pyridine, with its fairly basic

character, and its ability to form addition products, may influence the reaction mechanism. The reactions have now been carried out in a more inert solvent, *i.e.* a mixture of anisole and tetrahydrofuran. The hydrolytic agent was in some of these experiments tritiated water and in others a tritiated mixture of water and hydrochloric acid.

The water was present in at least ten-fold excess in all experiments and in the acid experiments the hydrogen chloride was present in twice the amount stoichiometrically needed. (The acid concentration in the acid-water mixture was about 18 % HCl by weight.) The technique was analogous to the one used earlier, *i.e.* the Grignard compound, dissolved in anisole-tetrahydrofuran, was added by means of an injection syringe or a dropping funnel to the water or the dilute hydrochloric acid, both dissolved in tetrahydrofuran. The anisole had been dried according to current methods, while the drying of the tetrahydrofuran was carried out by shaking it with anhydrous CaCl_2 , thereafter with metallic sodium and finally by distilling it from methylmagnesium iodide. After the preparation of the phenylmagnesium halide, a fraction of the solvent was distilled off at reduced pressure in order to eliminate benzene formed by moisture or other side reactions. The mixture of anisole and tetrahydrofuran in the proportion used

* Ref. ¹ is considered as part I.

Table 1. Results in the decomposition of Grignard compounds with water or hydrochloric acid at 20°C.

Grignard compound	Hydrolysis by	k_T/k_H	Number of parallel determinations of tritium in combustion water	Mean value (including error in determination of tritium in initial water)
CH_3MgI	water	0.700	2	0.71 ± 0.02
		0.713	2	
	hydrochloric acid	0.710	1	0.71 ± 0.04
		0.694	1	
$\text{C}_6\text{H}_5\text{MgI}$	water	0.738	1	
$\text{C}_6\text{H}_5\text{MgBr}$	water	0.644	1	$(0.64 \pm 0.04)^*$
		0.561	2	
	hydrochloric acid	0.570	1	0.57 ± 0.02
		0.579	2	
		0.567	1	0.57 ± 0.02

* Only one experiment.

dissolved the water or the hydrochloric acid, as well as the magnesium salts formed. The hydrocarbons produced were burnt over cupric oxide, and the radioactivity of the water formed, as well as that of the initial water used for the hydrolysis, was determined by means of a Geiger-Müller counter.

It should be noted that the yields of benzene from phenylmagnesium iodide were not very high. An experiment, done to find the approximate yield in the neutral hydrolysis, gave the result of about 20 %, determined by the method of isotope dilution. However, phenylmagnesium bromide seems to give better yields. In four of the five decompositions reported here the bromide was used.

The results, all obtained at 20°C, are given in Table 1. The reported values have not been corrected for the small change in the activity of the water or the

dilute hydrochloric acid occurring during the reaction.

Experiments were also done with *tert.*-butylmagnesium bromide. However, in this case, it was found to be impossible to use tetrahydrofuran as solvent, because it reacts instantly with the Grignard compound with evolution of heat and formation of a white precipitate, after which it will give no gas on admixture with water. Probably other branched chain alkylmagnesium halides will react in the same manner. It has been known for a long time that Grignard compounds react with ethylene oxide² and trimethylene oxide³.

1. Assarsson, L. O. *Acta Chem. Scand.* **9** (1955) 1399.
2. Blaise, E. E. *Compt. rend.* **134** (1902) 551.
3. Derick, C. G. and Bissell, D. W. *J. Am. Chem. Soc.* **38** (1916) 2484.

Received October 22, 1956.