

Identification of Products.— C_4F_{10} : This material was recovered from fractionation at between -1° and 1° . It had a molecular weight of between 238 and 240; analysis showed the absence of sulfur.

C_5F_{12} : This material was recovered from fractionation and boiled between 29 and 31° . Its molecular weight was between 286 and 288. It did not show the presence of sulfur. The crude fraction had a melting point range above 10° . Nuclear magnetic resonance spectra were made on aliquots of the sample and from the relative intensity of the CF_3 peaks, it was concluded that the sample contained neo- C_5F_{12} , iso- C_5F_{12} and n - C_5F_{12} , crudely in the ratio 3:2:1.

C_6F_{14} : This material boiled between 57 and 59° . It had a molecular weight of between 338 and 340. It contained no sulfur. The refractive index, n_D^{25} , was 1.2558.

C_7F_{16} : This material boiled between 82 and 83° . It had a molecular weight of 392. It contained no sulfur. The refractive index, n_D^{25} , was 1.2685.

Six grams of product boiled above 83° , and appeared to be fluorocarbon material.

Although the attack on the nickel packing was not too serious even at 518° , one trial, essentially the same as the third trial in the table, was made with the reactor filled with 0.125" NaF pellets. From this trial, 5 g. of C_4F_{10} , 2 g. of C_5F_{12} and 5 g. of C_6F_{14} were isolated and characterized. As only 3 g. of material boiled above 60° , no C_7F_{16} was isolated.

The author is grateful to Dr. F. W. Hoffman and Pvt. N. Muller, and the Army Chemical Center, Edgewood, Md., for the results of the NMR spectra, and to the chemistry Branch of the ONR (Nonr 580(03), NR 356-333) for the sponsorship of this work.

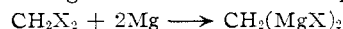
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Preparation and Reactions of Methylene- magnesium Dihalides

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RECEIVED AUGUST 2, 1955

During the course of another investigation it became necessary to prepare methylenedimagnesium dihalides (methylene di-Grignards). Both the dibromide and diiodide had been prepared previously by Emschwiller from the corresponding methylene halide, but the conversion of the magnesium was only of the order of 11%.¹ Chang and Chao-Lun Tseng have confirmed the preparation

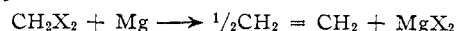


of the diiodide but state that the maximum yield is 10%.² We have succeeded in preparing methylenedimagnesium dibromide and methylenedimagnesium diiodide with conversions of the magnesium as high as 54%. The yield of the di-Grignard has been as high as 73%. A small amount of coupling

(1) G. Emschwiller, *Compt. rend.*, **183**, 665 (1926).

(2) D. Y. Chang and Chao-Lun Tseng, *Trans. Sci. Soc. China*, **7**, 243 (1932); *C. A.*, **26**, 5544 (1932).

accompanies this reaction, leading to the formation of ethylene.



The reactivity of the methylene di-Grignard reagent was found to be exceptionally low. No reaction was observed when an ethereal solution of benzaldehyde was heated to reflux for three hours with the di-Grignard reagent. The benzaldehyde was recovered quantitatively as the semicarbazone. When an ethereal solution of benzoyl chloride was heated to reflux for one hour with the reagent, there also was no reaction and the benzoyl chloride was recovered quantitatively as benzoic acid. A similar reaction with acetyl chloride, followed by hydrolysis, resulted only in the recovery of solvent from the organic layer. These results are in agreement with Chang and Chao-Lun Tseng who report no reaction with acetone, benzophenone, Michler ketone or carbon dioxide.²

Experimental

Methylenedimagnesium Diiodide.—Five grams (0.21 g. atom) of magnesium was covered with anhydrous ethyl ether. While the ether was heated under reflux and the magnesium stirred, 28.0 g. (0.11 mole) of methylene iodide, diluted with ten times its volume of anhydrous ether, was added dropwise over a period of 4.5 hours. After an additional hour of stirring, the flask was cooled and two layers formed. Hydrolysis of the lower layer gave 790 ml. (S.T.P.) of methane as confirmed by its infrared spectrum.³ The spectrum was recorded by the use of a 10-cm. cell at a gas pressure of approximately 760 mm. Gas which was collected in a cold trap (-196°) during the reaction was identified as ethylene by its vapor pressure.

The weight of unreacted magnesium indicated a 54% conversion of which 73% formed methylenedimagnesium diiodide while 27% went to the formation of ethylene. By decreasing the addition time of the methylene iodide to 1.5 hours, both the conversion and yield were reduced to 50%.

Methylenedimagnesium Dibromide.—The dibromide was prepared in the same manner as the diiodide. The addition of 19.0 g. (0.11 mole) of the methylene bromide solution required 15 minutes. Heating under reflux for three hours and the addition of a few crystals of iodine were necessary to initiate the reaction. In this case a 50% conversion of the magnesium was achieved, 58% of which formed methylenedimagnesium dibromide.

(3) The lower-membered di-Grignard reagents are insoluble in ether, forming a lower layer. A. Kreuchunas, *THIS JOURNAL*, **75**, 3339 (1953), reports that the solubility increases with chain length and that the C_{10} -compound does not form a separate layer.

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The Effect of Liquid Ammonia on Proteins. I. Insulin

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RECEIVED JUNE 3, 1955

In order to evaluate the use of non-aqueous solvents for tissue fractionation, preliminary experiments were carried out with the insulin-liquid ammonia system¹ employing samples of high potency insulin with known physical chemical properties. These experiments indicated that long exposures of insulin to liquid ammonia did not alter any physical chemical properties as judged by solubility, sedi-

(1) E. Ellenbogen, Abstr. 124th National Meeting, American Chemical Society, page 20 C, 1953.