

general are concerned, then one may conclude that the limiting factor in the synthesis of ammonia is not the rate of activation of the hydrogen but the rate at which the nitrogen molecule can be brought into a reactive form by the catalyst.

Benton and White [THIS JOURNAL, 53, 3301 (1931)] have pointed out that activated adsorption of hydrogen on a sample of this same iron catalyst begins between -78° and about 0° . The results obtained in the present research seem entirely consistent with their conclusion. The study of the kinetics and temperature coefficient of the para-ortho hydrogen conversion on various synthetic ammonia catalysts is being continued.

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THE ALLYLIC REARRANGEMENT OF CROTYL BROMIDE AND CROTYL-MAGNESIUM BROMIDE

Sir:

In view of the recent appearance of an article by Gilman and Harris¹ on the allylic rearrangement of cinnamylmagnesium chloride, it seems advisable to present a preliminary report on the allylic rearrangement of crotylmagnesium bromide.

Using the method of Dillon, Young and Lucas² we have analyzed butenes obtained from the following steps: *trans*-crotonaldehyde \rightarrow crotyl alcohol \rightarrow crotyl bromide \rightarrow 2-butene. The 2-butenes obtained by the action of (a) zinc and aqueous alcohol on crotyl bromide and (b) dilute acid on crotylmagnesium bromide, both contained approximately 10% 1-butene. This was contrary to our expectations since crotyl bromide, according to the work of Prévost³ and Bouis⁴ should be free from α -methylallyl bromide and thus give pure *trans*-2-butene. The presence of 1-butene in these mixtures must be attributed to an allylic rearrangement of the crotyl bromide or of the Grignard reagent and the corresponding zinc compound. Recent work in this Laboratory on crotyl alcohol and work on 2-pentene-1-ol by Meisenheimer and Link⁵ indicates that an allylic transformation probably does occur during the preparation of the bromide. For example, the boiling ranges of different crotyl bromide preparations vary from 1–12° depending on the procedure used.

¹ Gilman and Harris, THIS JOURNAL, 53, 3541 (1931).

² Dillon, Young and Lucas, *ibid.*, 52, 1953 (1930).

³ Prévost, *Ann. chim.*, [10] 10, 147–181 (1928).

⁴ Bouis, *Bull. soc. chim.*, [4] 41, 1160 (1927).

⁵ Meisenheimer and Link, *Ann.*, 479, 260 (1930).

In order to determine whether or not an allylic transformation also results during the formation of the Grignard reagent, we have converted all of these bromide preparations containing variable quantities of α -methylallyl bromide, into the magnesium compound under identical conditions. The resulting butene mixtures should be of constant composition regardless of the composition of the bromides if an allylic equilibrium is involved; if not, the butene mixtures should have compositions corresponding to those of the bromide preparations. The results of these experiments will be available in the near future.

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TESTS FOR ELEMENT 87 (VIRGINIUM) BY THE USE OF ALLISON'S MAGNETO-OPTIC APPARATUS

Sir:

In December, 1930, one of us (McGhee) handed out by number to Professor Allison twelve (to him) "unknowns" which were tested by him and checked by two assistants 100% correctly in three hours. The improved model of his machine which was later installed in our laboratory under Dr. Allison's direction has been proved to be reliable by numerous tests on known solutions of pure substances. No two, different, metallic salts of the same acid produce minima that coincide. Hence we read with interest the footnote to an article by Papish and Wainer [THIS JOURNAL, 53, 3818 (1931)] in which it was suggested that "solutions of SnCl_4 and ReCl_2 gave minima which were coincident with those obtained for element 87," possibly due to the formation of the complex ions, SnCl_3^+ and ReCl^+ .

To test this question, hydrochloric acid solutions of the minerals samarskite, pollucite and lepidolite, and of crude cesium chloride were made up. Element 87 (Virginium) had been reported in all of them. When observations were made on these solutions within the scale limits between which ViCl would fall, twelve minima were found. Similar observations on the sulfates of the minerals yielded only six minima. Since the same number of minima are always found for any one metal, no matter to which acid radical it might belong, it was thought that six of the minima appearing in the chloride region might indeed be due to ReCl^+ and SnCl_3^+ . With this in view, a solution of pure SnCl_4 was made up and examined for minima. In addition to the minima of SnCl_4 previously determined, four minima at 44.20, 44.40, 44.98, 46.06 were found. Likewise a solution of ReCl_2 (obtained by adding hydrochloric acid to pure potassium perhenate) was examined for minima. Beside those previously attributed