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On the Continuous Preparation of Vinyl Grignard Reagents

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In 1934 H. Normant[2] showed that vinylmagnesium bromide could be prepared in good yields using tetrahydrofuran as a solvent. In many subsequent publications Normant and co-workers demonstrated the syntheses of several vinyl derivatives.[3] Recently, Ramsden, *et al.*,[4] have shown the generality of Normant's method by extending it to vinyl chloride. Since then, vinylmagnesium halides have been used extensively in the syntheses of olefinic derivatives.

Recent investigations in this laboratory have been concerned with the syntheses of new vinyl compounds. During the course of this work considerable quantities of vinylmagnesium halides, primarily vinylmagnesium chloride, had to be prepared. In order to avoid large batch operations and still maintain an economical procedure, a continuous process has been developed and employed. This not only afforded a convenient method of preparing the vinyl Grignard reagents, but also circumvented possible side reactions by maintaining a permanent excess of magnesium and removing the changed vinyl chloride essentially quantitatively.

The process may best be described by referring to Fig. 1 which shows the design and construction of the apparatus for operations on a laboratory scale.

EXPERIMENTAL

Vinyl chloride was fed into the apparatus of Fig. 1 at *g* having the stopcock *b* adjusted in such a way that the gas passed through vessel *E*. *E* served as a bubble counter. The end of the feed tube was immersed in a few milliliters of tetrahydrofuran, saturated with vinyl chloride. Having the stopcocks *c* and *a* appropriately adjusted, the gas was allowed to pass through the second of the three concentric tubes, which were the principal parts of the absorption column *A*. The gas left this tube from the bottom and then entered the inner tube which was packed with 6-mm. Raschig rings. In this tube the gas was absorbed by tetrahydrofuran, addition of which was maintained at a constant rate from the supply container *G*. The vinyl chloride–tetrahydrofuran solution rose in the outer tube of *A* which ran over into the inner tube of the reaction apparatus *B* which was also composed of three concentric tubes. This inner tube of *B* was filled with magnesium turnings. The reaction occurred while flowing through this tube. To keep the system at the required temperature and to carry off the exothermic heat, water, thermostatically controlled at 50–52°, was pumped through the second tube.

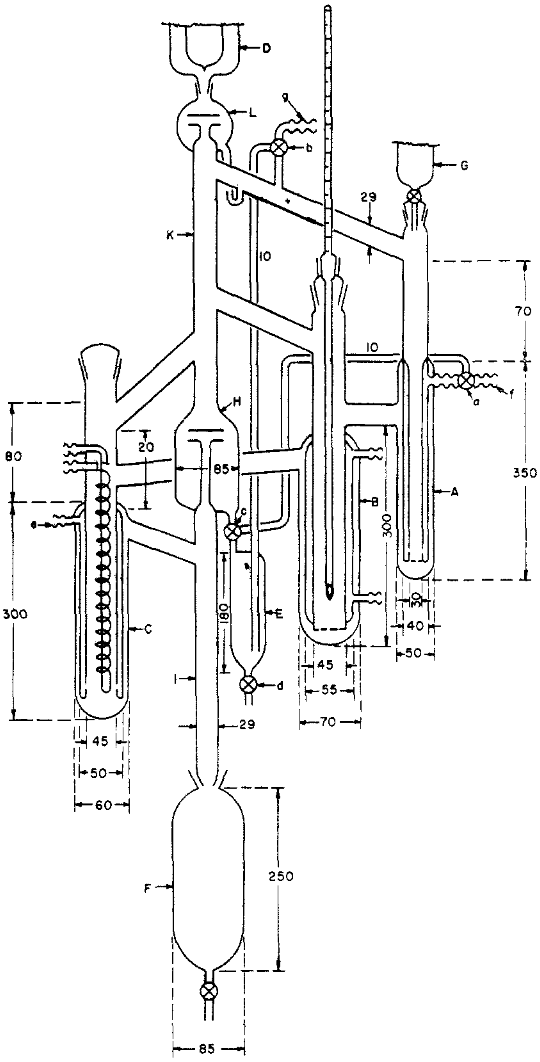

Fig. 1. Apparatus for the continuous preparation of vinyl Grignard reagents. Units are millimeters

The reaction solution rose in the outer tube and passed into the inner tube of *C*. *C* again consisted of three concentric tubes. Nitrogen was introduced at *e*, left the middle tube at the bottom, and entered the inner tube. Passing through the reaction mixture, the nitrogen removed the unchanged vinyl chloride and a part of the tetrahydrofuran. Both the vinyl chloride and the tetrahydrofuran were then condensed from the gas in the condenser *D*, which was charged with a carbon dioxide–acetone mixture. Due to

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[2] H. Normant, *Compt. rend.*, **239**, 1510 (1954).

[3] (a) H. Normant, *Compt. rend.*, **239**, 1811 (1954); **240**, 314, 440, 631, 1111, 1435 (1955). (b) H. Normant and C. Crisan, *Compt. rend.*, **240**, 1946 (1955). (c) H. Normant and P. Maitte, *Bull. soc. chim. France*, 951, 1439 (1956). (d) H. Normant and J. Ficini, *Bull. soc. chim. France*, 1441 (1956). (e) J. Ficini, *Bull. soc. chim. France*, 119 (1956). (f) V. Levy and H. Normant, *Compt. rend.*, **242**, 202 (1957). (g) H. Normant and G. Martin, *Bull. soc. chim. France*, 429, 728 (1957).

[4] Hugh E. Ramsden, *et al.*, *J. Org. Chem.*, **22**, 1602 (1957).

the special design of L the condensed liquids were fed back into the inner tube of A. The concentration of the reaction solution could be altered by varying the rate of flow of the nitrogen. The temperature of the solution could be regulated by means of the built-in cooling spiral. The prepared Grignard solution rose in the outer tube of C and was fed *via* I into the container F. From here it was bottled under nitrogen. A certain amount of tetrahydrofuran was condensed in K and collected in H. This condensate was periodically drained into E. By appropriate adjustments of stopcocks a, b, and c the condensate was forced into the inner tube of A by nitrogen introduced at f.

In the manner described, the conversion of 24 g. of magnesium to 0.5 to 2.5M vinylmagnesium chloride solutions was accomplished within 6–7 hr. The preparation of these solutions could be interrupted arbitrarily and started again without any difficulties. The magnesium consumed by the reaction was replenished periodically. A special activation of this magnesium was not necessary when vinylmagnesium chloride solution was present. In other cases the reaction could be easily initiated by addition of small quantities of ethyl bromide or, still better, vinyl Grignard reagent.

The yields, determined by a modification of the Gilman titration as reported by Ramsden, *et al.*,[4] were found to be in the range of 96 to 98% with respect to vinyl chloride.

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