

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

A QUANTITATIVE STUDY OF THE REACTION BETWEEN  
ETHYLENIC HYDROCARBONS AND THE GRIGNARD REAGENTBY HENRY GILMAN AND H. MARJORIE CRAWFORD<sup>1</sup>

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## Introduction

In connection with a series of studies of the mechanism of reaction between the Grignard reagent and compounds having more than one reactive group, it was necessary to determine whether RMgX compounds add to an ethylenic linkage. In a qualitative investigation Blaise<sup>2</sup> attempted to bring about a reaction between the Grignard reagent and 2 olefinic hydrocarbons, caprylene and hexylene, but was unsuccessful. The work of Kohler and co-workers,<sup>3</sup> Reynolds,<sup>4</sup> Blaise and Courtot,<sup>5</sup> and others on the interaction of the Grignard reagent and unsaturated carbon compounds indicates an apparent addition to the ethylenic linkage. In all these cases, however, we are dealing with 1,4-addition, and the apparent 1,2-addition to the ethylenic linkage is due to the rearrangement of the enol that results when the addition product is decomposed by acids. Gilman and Heckert,<sup>6</sup> in a study of the mechanism of reaction between ketenes and the Grignard reagent, proved that addition does not take place at the ethylenic linkage.

The Grignard reagent is known to react with some ethylenic hydrocarbons. However, this reaction is not one of addition, and it has been shown<sup>7</sup> to consist in the replacement of a so-called active hydrogen by the —MgX group.

There is at present no definite general knowledge as to whether the Grignard reagent will add to the double bond in ethylenic hydrocarbons. Recent work by Lespieau<sup>8</sup> assumes that such addition does take place, and the formation of a reaction product is interpreted on this basis. In a paper which has just appeared, Staudinger, Kreis and Shilt<sup>9</sup> explain the formation of a hydrocarbon by likewise assuming addition of the Grignard reagent to an ethylenic linkage. To justify such an interpretation they speak of it as a reaction which has "often been observed." One of us called attention in an earlier paper<sup>6</sup> to the fact that there were no known cases

<sup>1</sup> This paper is an abstract of a thesis presented by H. M. Crawford in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

<sup>2</sup> Blaise, *Compt. rend.*, **132**, 38 (1901).

<sup>3</sup> Kohler and others, *Am. Chem. J.*, **31**, 642 (1904), etc.

<sup>4</sup> Reynolds, *ibid.*, **46**, 198 (1911).

<sup>5</sup> Blaise and Courtot, *Compt. rend.*, **140**, 370 (1905).

<sup>6</sup> Gilman and Heckert, *THIS JOURNAL*, **42**, 1010-1014 (1920).

<sup>7</sup> Comanducci, *Rend. accad. sci. Napoli*, **4**, 245-8 (1908); *C. A.*, **4**, 2264 (1910).

<sup>8</sup> Lespieau, *Bull. soc. chim.*, **29**, 883 (1921).

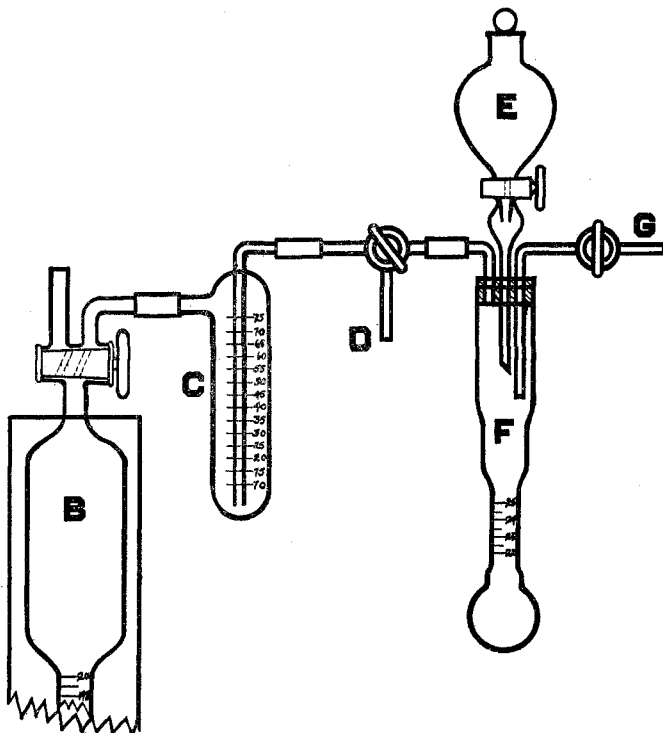
<sup>9</sup> Staudinger, Kreis and Shilt, *Helvetica Chim. Acta*, **5**, 743 (1922).

in which the Grignard reagent combined directly with an ethylenic linkage. A review of work done since that time has disclosed nothing that would warrant alteration of that finding.

With methods now available for quantitatively estimating the Grignard reagent, an exact study has been made of the reaction between the Grignard reagent and a variety of hydrocarbons having one or more ethylenic linkages. It is shown that the Grignard reagent will not add to an ethylenic linkage. This applies not only to the ordinary conditions where the compound is digested with an equivalent of  $\text{RMgX}$  compound in ether solution, but also to a run in which 1,1-diphenyl-ethylene was refluxed for 35 hours with 6 equivalents of ethylmagnesium iodide, and to another experiment where 1,4-diphenyl-butadiene was refluxed with ethylmagnesium iodide at the boiling point of *n*-butyl ether.

### Procedure

An aliquot portion of ethylmagnesium iodide was forced by hydrogen pressure into the graduated flask F, and by use of the gas-analysis method



previously described<sup>10</sup> the strength of this solution was determined on the basis of ethane evolved. Repeated check analyses showed that the

<sup>10</sup> THIS JOURNAL, 45, 150 (1923).

standard solution did not vary in strength even on extensive refluxing.

The unsaturated hydrocarbon, in slightly more than sufficient quantity to react with all of the ethylmagnesium iodide used in a given run, was added to the known amount of Grignard reagent. The flask was then attached to a reflux condenser, provided with drying tubes containing soda-lime and phosphorus pentoxide, and the mixture boiled, generally for 15 minutes. After refluxing was complete, the flask was connected to the apparatus as shown in the diagram, and dry ether was passed in at G and out at D. When the gas issuing from D was completely absorbed by conc. sulfuric acid contained in an inverted test-tube arrangement, thus proving that all air had been displaced, the stopcock at G was closed and the stopcock at D turned to connect the flask with the sulfuric acid washer C and the gas buret B.

Using the technique and making the corrections already described,<sup>10</sup> the volume of ethane liberated when dil. sulfuric acid was run from the separatory funnel (E) into the mixture contained in F was readily ascertained. For purposes of comparison all calculations were made on the

TABLE I  
RESULTS OF GAS ANALYSES

Compound used	Average corr. vol. of C <sub>2</sub> H <sub>6</sub> from 20 cc. of C <sub>2</sub> H <sub>5</sub> MgI sol.	Compound used	Average corr. vol. of C <sub>2</sub> H <sub>6</sub> from 20 cc. of C <sub>2</sub> H <sub>5</sub> MgI sol.	Compound used	Average corr. vol. of C <sub>2</sub> H <sub>6</sub> from 20 cc. of C <sub>2</sub> H <sub>5</sub> MgI sol.
	Cc.		Cc.		Cc.
C <sub>2</sub> H <sub>5</sub> MgI solution..	200.4	Phellandrene <sup>14</sup> .....	177.8	1,1 - diphenyl <sup>14,17</sup>	
Ethylene <sup>11</sup> .....	205.3	1,1-diphenyl <sup>14,15</sup>		amylene.....	142.2
Amylene.....	196.7	ethylene.....	181.8	1,4 - diphenyl <sup>18</sup>	
Diallyl.....	196.3	1,1 - diphenyl <sup>14,16</sup>		butadiene.....	201.7
Cyclohexene <sup>12</sup> ....	195.3	propylene.....	175.0	Tetraphenyl-ethyl-	
Cyclohexadiene <sup>13</sup> ...	193.9			ene.....	198.9

<sup>11</sup> The ethylene, dried by phosphorus pentoxide, was bubbled through the Grignard solution during the 15-minute period of refluxing.

<sup>12</sup> When the mixture was refluxed for 30 minutes, the average volume of ethane was 194.9 cc.

<sup>13</sup> The authors wish to acknowledge gratefully the kindness of E. C. Kendall and A. E. Osterberg of the Mayo Laboratories in providing this compound.

<sup>14</sup> See Discussion.

<sup>15</sup> When this mixture was refluxed for 30 minutes the volume dropped to 170.6 cc.; and when it was refluxed for 45 minutes the volume was 151.8 cc.

<sup>16</sup> Prepared from benzophenone and ethylmagnesium bromide.

<sup>17</sup> 1,1-Diphenyl-amylene was prepared from benzophenone and *n*-butylmagnesium bromide, the corresponding carbinol readily losing water during distillation; b. p. 297–301°; *n*<sub>D</sub><sup>20</sup>, 1.5888; *d*<sub>4</sub><sup>20</sup>, 1.0917.

Calc. for C<sub>17</sub>H<sub>18</sub>: C, 91.89; H, 8.11. Found: C, 91.83, 91.65; H, 8.16, 8.00.

<sup>18</sup> When this mixture was refluxed for 15 minutes in *n*-butyl ether, the average volume of ethane was 180.5 cc. Under corresponding conditions a like volume of ethylmagnesium iodide alone gave 182.1 cc. of ethane.

basis of a 20cc. aliquot portion of standard ethylmagnesium iodide solution. Several analyses were made with each hydrocarbon.

It is obvious that if the volume of ethane evolved from an aliquot of Grignard reagent is essentially the same after treatment with unsaturated hydrocarbon as before then no addition to the ethylenic linkage can have taken place.

### Discussion

When the quantitative work was ended, it appeared that phellandrene and 1,1-diphenyl-ethylene, -propylene, and -butylene had added ethylmagnesium iodide. The variations with the other hydrocarbons from the volume of ethane given by the Grignard reagent alone are sufficiently small, comparatively, to justify the conclusion that these hydrocarbons do not add ethylmagnesium iodide under the conditions described.

In order to determine the mode of addition of the Grignard reagent to 1,1-diphenyl-ethylene, this hydrocarbon was refluxed in ether solution for several hours with one equivalent of ethylmagnesium iodide. The reaction product when worked up in the customary manner appeared to consist almost entirely of unchanged ethylenic hydrocarbon. Acting on the belief that the treatment was not sufficiently vigorous, we refluxed one equivalent of 1,1-diphenyl-ethylene in ether solution with 6 equivalents of ethylmagnesium iodide for 35 hours. The reaction product of this experiment again consisted essentially of unchanged hydrocarbon, and a rapid titration with standard bromine-benzene solution showed practically no difference in unsaturation between untreated 1,1-diphenyl-ethylene and that which was obtained after the 35-hour period of refluxing.

Because of the similarities in structure, mode of preparation and behavior towards the Grignard reagent of 1,1-diphenyl-ethylene, -propylene, and -butylene, and because tetraphenyl-ethylene which is a related "1,1-diphenyl" hydrocarbon showed no apparent reaction, it was inferred that some impurity might be contained in the 3 first mentioned hydrocarbons which would account for the drop in volume of ethane observed. This inference received complete substantiation when each of them was found to contain small amounts of benzophenone, identified in each case by the preparation of the corresponding oxime and mixed-melting-point determinations with known benzophenone-oxime. The 1,1-diphenyl-ethylene recovered after the protracted digestion with ethylmagnesium iodide gave no oxime.

The presence of benzophenone in each of these hydrocarbons is due to unchanged ketone left after the Grignard reaction used for their preparation. Because benzophenone boils at 306° and the three hydrocarbons mentioned boil within less than 30° of it, a very careful fractionation is necessary to insure a complete separation.

These several experiments emphasize two points. First, in the preparation of unsaturated hydrocarbons from aldehydes or ketones and the Grignard reagent it is desirable to use a slight excess of the latter. Second, the Grignard reagent can apparently be used with advantage in the purification of an ethylenic hydrocarbon when the suspected impurity is a compound with a carbonyl group.

No oxime could be prepared from the phellandrene used in this work. However, the compound very likely contained a small quantity of impurity which added ethylmagnesium iodide. This assumption is borne out, in large part, by an experiment made subsequent to the gas analysis, when phellandrene was refluxed in ether solution with 3 equivalents of ethylmagnesium iodide for 8 hours. On working up the reaction product in the customary manner, practically all of the phellandrene was recovered.

A study is now in progress of the reaction between disubstituted acetylenic hydrocarbons and the Grignard reagent.

### Summary

It is shown that ethylmagnesium iodide does not add to several typical ethylenic hydrocarbons under varying conditions.

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### NEW BOOKS

**Inorganic Chemical Synonyms and Other Useful Chemical Data.** By ELTON RICHMOND DARLING, Professor of Chemistry, James Millikin University, Decatur, Illinois. Second edition, revised and enlarged. D. Van Nostrand Company, 8 Warren Street, New York, 1922. vii + 119 pp. 18.5 × 11.5 cm. Price \$1.00 net.

The appearance of this book in a second edition indicates that it is filling a real need. This is not astonishing when consideration is given to the number of business men who in recent years have turned to books for information about chemistry.

To the condensed information regarding the elements, their discovery and the various names of their compounds given in the first edition, the author has now added 3 sections of comparatively great value; first, about 150 names of ores of technical importance with their formulas, classified by their valuable elements; second, 3 pages listing the physical properties of the metals, including atomic volume, specific gravity, specific heat, melting point (on both Centigrade and Fahrenheit scales), coefficient of linear expansion, thermal conductivity referred to silver and electrical conductivity referred to mercury; third, multiples of the atomic weights of the elements. These additions should increase the usefulness of the book greatly. Additions have also been made to the two lists of chemical synonyms.