perature coefficient, the effect being especially pronounced for 1:5 mixtures. At 200 mm. the temperature coefficient for the 1:1 mixture was 1.6×10^4, the lowest reaction temperature 286°. At 300 mm. the temperature coefficient for the 1:5 mixture was only 1.0×10^4, and the lowest reaction temperature 345°.

A reasonable explanation would be that, as the pressure is lowered, a surface reaction becomes predominant over a gas phase reaction. To test this, runs were made with a bulb packed with bits of broken Pyrex. However, at 600 mm. with a 1:5 mixture, the reaction was found to have the high temperature coefficient 3.5×10^4. This does not deny the above hypothesis, for at the same time the lowest reaction temperature was raised to 403°, so that even though the surface had been increased many-fold the homogeneous reaction with its higher temperature coefficient could still be predominant.

When runs were made in an empty bulb, the walls of which had been coated with potassium chloride, the pressure rose gradually from the very beginning of each experiment. For this reason one cannot compare the 5% times of these runs with those of the previous sets. Nevertheless, judging from the temperature range over which the reaction could be observed, a high temperature coefficient probably obtained here also. The lowest temperature of reaction was 289° for a 1:1 mixture at 700 mm. Thus the potassium chloride coating inhibits the reaction at low, but not at high temperatures.

It was interesting to note in several instances during this work the appearance of several consecutive rapid reactions after a long induction period, just as was reported by Thompson and Kelland [*J. Chem. Soc.*, 1809 (1931)] in the case of the oxidation of hydrogen sulfide.

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[CONTRIBUTION NO. 44 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

The Behavior of Unsaturated Hydrocarbons toward the Grignard Reagent at Elevated Temperatures

BY CORLISS R. KINNEY AND ROBERT G. LARSEN

Occasionally assumptions have been made that Grignard reagents add to ethylenic or acetylenic linkages. These assumptions have been most conclusively refuted by Gilman and co-workers.[1] In addition they have made several exhaustive studies of the behavior of the Grignard reagent toward ethylenic and acetylenic hydrocarbons, over thirty hydrocarbons being included.[2] Several additional hydrocarbons have been studied by Wieland and Krause,[3] and by Wilson and Hyslop.[4] In all of this work no reaction was observed to take place between reagent and unsaturated hydrocarbon. These experiments, however, were carried out at temperatures not exceeding the boiling point of the ether solutions of the reagents; consequently, we have extended the work to higher temperatures to determine whether the reaction might be induced under such conditions.

Gilman and associates[2a,b,c] proved that ethyl magnesium bromide failed to react with the unsaturated hydrocarbons by showing that just as much ethane was liberated, by treatment with water, from aliquot portions of the reagent after contact with the hydrocarbon as before. This method is unsuited for use at higher temperatures because the reagent will decompose if heated too strongly. Therefore, phenylmagnesium bromide and several unsaturated hydrocarbons were chosen which would yield crystalline products if a reaction took place.

The phenylmagnesium bromide was prepared in the usual way in ether solution and in a four to one ratio to the hydrocarbon which was to be added. The hydrocarbon was dissolved in one of several higher boiling solvents; xylene, diphenyl, diphenyl ether and a fraction of kerosene, all were used. The resulting solution was added to the Grignard reagent and the mixture distilled until the

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[1] (a) Gilman and Heckert, THIS JOURNAL, **42**, 1010 (1920); (b) Gilman and Harris, *ibid.*, **49**, 1825 (1927); (c) Gilman, Kirby, Fothergill and Harris, *Proc. Iowa Acad. Sci.*, **54**, 221 (1928); *C. A.*, **22**, 4504 (1928); (d) Gilman and Schulz, THIS JOURNAL, **52**, 3588 (1930); (e) Gilman and Kirby, *ibid.*, **54**, 345 (1932).

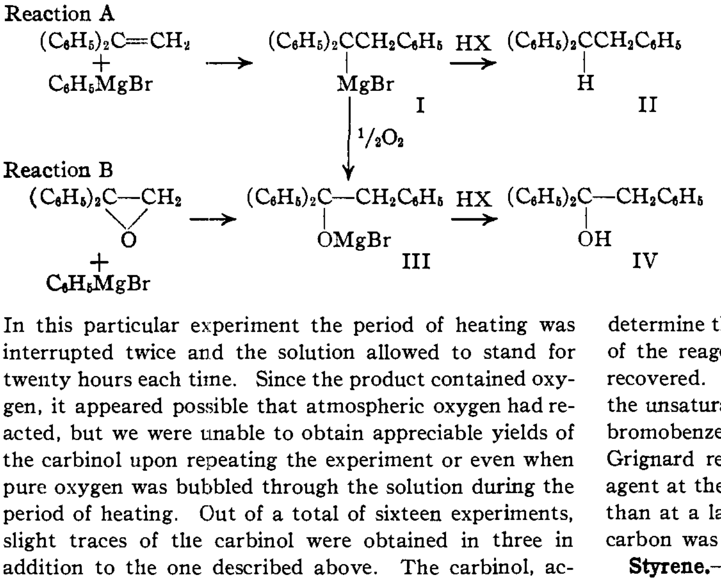
[2] (a) Gilman and Crawford, *ibid.*, **45**, 554 (1923); (b) Gilman and Shumaker, *ibid.*, **47**, 514 (1925); (c) Gilman and Peterson, *ibid.*, **48**, 423 (1926); (d) Gilman and McGlumphy, *Rec. trav. chim.*, **47**, 418 (1928).

[3] Wieland and Krause, *Ann.*, **443**, 129 (1925).

[4] Wilson and Hyslop, *J. Chem. Soc.*, **123**, 2612 (1923); **125**, 1556 1924).

temperature rose to the desired point, measured by a thermometer inserted in the liquid. The mixture was stirred and heated for at least eight hours. It was then poured upon cracked ice and sulfuric acid. The organic material was separated and subjected to steam distillation, vacuum fractionation, fractional crystallization or extraction with petroleum ether, attempting to isolate crystalline products of a reaction. Attempts were also made to separate, by the use of concentrated sulfuric acid, unsaturated and oxygenated compounds from any saturated hydrocarbon products that might be present. In other experiments the unchanged hydrocarbon was recovered as quantitatively as possible.

α,α-Diphenylethylene.—In one of the preliminary experiments on α,α-diphenylethylene at 135° in xylene solution a 15% yield of diphenylbenzylcarbinol IV was obtained. Obviously the substance was not a primary product of the reaction because it contained oxygen. It is, however, possible to write a reaction involving addition of the Grignard reagent to the unsaturated hydrocarbon to account for this product. This reaction, together with another which seems more likely, appears below.



In this particular experiment the period of heating was interrupted twice and the solution allowed to stand for twenty hours each time. Since the product contained oxygen, it appeared possible that atmospheric oxygen had reacted, but we were unable to obtain appreciable yields of the carbinol upon repeating the experiment or even when pure oxygen was bubbled through the solution during the period of heating. Out of a total of sixteen experiments, slight traces of the carbinol were obtained in three in addition to the one described above. The carbinol, according to reaction A, would be preceded by the magnesium derivative I which upon decomposition by acid would yield the saturated hydrocarbon II. However, no trace of that hydrocarbon was obtained, and we came to the conclusion that, since the Grignard reagent reacts very slowly with oxygen when protected from the air by a layer of refluxing solvent[5] there must have been considerable quantities of the magnesium derivative I present in order to form the carbinol, and since no trace of the saturated hydrocarbon II was observed in any of the products reaction A must be incorrect.

In reaction B, α,α-diphenylethylene oxide is assumed to have been present in the α,α-diphenylethylene. This substance was made by dehydrating diphenylmethylcarbinol which in turn was made by the reaction of methylmagnesium iodide on benzophenone. The diphenylmethylcarbinol was not purified before the dehydration process, but the entire product of the Grignard reaction was dehydrated in air to about 125°, at which point vapors of iodine appeared. The material was washed with sodium bisulfite solution to remove the iodine and after separation from the solution was vacuum distilled. The hydrocarbon distilled quite constantly at 156° at 9 mm. pressure and was obtained in an 81% yield. Although it is not possible to state with certainty that the original sample of α,α-diphenylethylene contained the oxide, it seems more likely than that in one experiment out of a total of sixteen the Grignard reagent reacted with the unsaturated hydrocarbon followed by a nearly quantitative reaction with molecular oxygen.

In addition to the reactions at 135° in xylene solution, two were attempted at 150° in kerosene and in diphenyl, respectively, two in diphenyl ether at 180° and at 195° and finally one in kerosene in a sealed tube at 300–325°. Since it is possible that the Grignard reagent reacted with the diphenyl ether at the temperatures employed, a blank run was made on the ether at 200° for a period of three hours. Under these conditions the reaction proceeded in exactly the same fashion as when the hydrocarbon was present, a viscous red oil separating from the solution. Upon decomposing the mixture in the usual way and extracting the product with sodium hydroxide, 0.5 g. of phenol was obtained, which showed that very little reaction had taken place between the reagent and the diphenyl ether or atmospheric oxygen. The presence of considerable tarry residue indicated that a part at least of the reagent had been decomposed. In the sealed tube reaction at 300–325° the reagent was obviously largely decomposed and no test was made to determine the extent, but in spite of the increased activity of the reagent 92% of the unchanged hydrocarbon was recovered. Also an experiment was carried out in which the unsaturated hydrocarbon was added together with the bromobenzene during the course of the preparation of the Grignard reagent, based on the assumption that the reagent at the moment of formation might be more reactive than at a later time. However, over 95% of the hydrocarbon was recovered unchanged.

Styrene.—Three experiments on styrene were conducted in xylene solution at temperatures ranging from 130 to 160°. Considerable polymerization occurred, but it was not complete at all. No trace of α,α- or α,β-diphenylethane was isolated from the products.

Methylphenylacetylene.—Methylphenylacetylene was heated in xylene solution at 130° and, as before, no product of a reaction was isolated.

Trimethylphenylallene.—After refluxing trimethylphenylallene in xylene at 130° for ten hours, nearly 90% of the unsaturated hydrocarbon was recovered. Except for a small quantity of diphenyl and a small tarry residue, no other substance was present in the fraction boiling above the xylene.

Summary

No direct evidence was obtained for the addition of phenylmagnesium bromide to α,α-

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[5] Goebel and Marvel, THIS JOURNAL, **55**, 1694, line 11 (1933).

diphenylethylene, styrene, methylphenylacetylene and trimethylphenylallene at temperatures ranging from 130 to 300°.

SALT LAKE CITY, UTAH RECEIVED DECEMBER 8, 1934

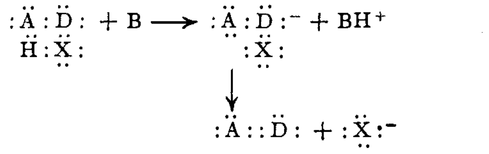
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

The Removal of Hydrogen and Acid Radicals from Organic Compounds by Means of Bases. I. The Removal of Hydrogen Chloride from Ald-chlorimines by Sodium Hydroxide. Rates of Reaction in Alcoholic Solution[1]

BY CHARLES R. HAUSER, JOHN W. LEMAISTRE AND A. E. RAINSFORD

Recently, several independent workers have suggested that in the removal of HX (where X is halogen, acetate, etc.) from certain organic compounds by means of bases, a proton is removed first, followed by the release of X with a complete octet of electrons. This mechanism has been proposed by Drake and McElvain[2] for the removal of hydrogen bromide from ethyl β-bromopropionate in the presence of piperidine, and by Mills[3] for the removal of acetic acid from β-aldoxime acetates in the presence of alkali. It has been suggested[4] that the removal of hydrogen chloride from ald-chlorimines by various bases also follows this course.

This mechanism appears to be a satisfactory hypothesis for classifying a number of reactions brought about by bases. The removal of HX from various compounds which may be regarded as belonging to the type $\begin{array}{l}:\ddot{A}:\ddot{D}:\\ \;\ddot{H}:\underset{..}{\ddot{X}}:\end{array}$ or $\begin{array}{l}:A::D:,\\ \;\ddot{H}\;:\underset{..}{\ddot{X}}:\end{array}$ where A and D are carbon, nitrogen or oxygen, in the presence of a base B, might be represented by the general equation[5]



$$\begin{array}{lll} \begin{array}{l}:\ddot{A}:\ddot{D}:\\ \;\ddot{H}:\underset{..}{\ddot{X}}:\end{array} + B & \longrightarrow & \begin{array}{l}:\underset{..}{\ddot{A}}:\ddot{D}:^- + BH^+\\ \qquad :\underset{..}{\ddot{X}}:\end{array} \\ & & \qquad\downarrow \\ & & :\ddot{A}::\ddot{D}: + :\underset{..}{\ddot{X}}:^- \end{array}$$

Several examples have already been mentioned.[6] Alkali removes HX from compounds of the type RCH═NX, where X is halogen, acetate, 2,4-dinitro-,[7] or 2,4,6-trinitrophenoxy.[8]

In this paper are reported the results of a study of the rates of reaction of ald-chlorimines with sodium hydroxide in which the yields of nitriles are practically quantitative. Bimolecular velocity constants have been determined at 0° for seventeen chlorimines in 92.5% alcohol and for four chlorimines in a 50% dioxane–water mixture. Constants have been determined also at 30° for five chlorimines in 92.5% alcohol, and the temperature coefficients and heats of activation for the reactions calculated.

Experimental

Solvents. Commercial ethyl alcohol (95% by volume) was distilled through a four-bulb fractionation column. The portion boiling at 78.1 ± 0.02° was used in this work. This solvent contained 92.5% ethyl alcohol by weight: d^{20}_4 0.8111.

Commercial dioxane was distilled through a four-bulb column. The fractions freezing below 11.0° were rejected. The distilled product (f. p. 11.0–11.2°) was mixed with an equal weight of water to give the 50% dioxane used in this work.

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[1] This paper is in part from a thesis presented by J. W. LeMaistre in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Duke University.

[2] Drake and McElvain, THIS JOURNAL, **56**, 699, 1810 (1934). It is stated in a note of a paper by Noller and Dinsmore [*ibid.*, **54**, 1032 (1932)] that a referee suggested that the removal of hydrogen bromide from alkyl bromides by pyridine may consist of the incipient withdrawal of a hydrogen ion, which would promote the liberation of halide ion. Very recently, Olivier [*Rec. trav. chim.*, **53**, 1093 (1934)] has proposed a similar mechanism for the removal of hydrogen halide from ethylene dibromide and other aliphatic halides in the presence of alkali. See also, Michael, THIS JOURNAL, **42**, 818 (1920). A similar mechanism has been used to explain the alkaline hydrolysis of certain sulfonamides and the decomposition of quaternary ammonium hydroxides. See Ingold and co-workers, *J. Chem. Soc.*, 1305 (1926); 997 (1927); 526 (1933).

[3] Mills, *J. Soc. Chem. Ind.*, **51**, 750 (1932). For complete mechanism see original paper.

[4] Hauser and Moore, THIS JOURNAL, **55**, 4526 (1933), and A. G. Gillaspie, M.A. Thesis, Duke University, 1930.

[5] A similar concept may be applicable to the removal of HX from compounds of the type $\begin{array}{l}\;\;\mathrm{H}\\ :\underset{..}{\ddot{A}}:\underset{..}{\dot{X}}:\end{array}$ where A is carbon or nitrogen.

[6] Verhoek [THIS JOURNAL, **56**, 576 (1934)] has suggested that the trichloroacetate ion decomposes to form CO_2 and $(CCl_3)^-$, and that the latter reacts with water to form chloroform. On this basis, the reaction of trichloroacetic acid with a base might be regarded as involving the removal of HX, where X is CCl_3. Likewise, the removal of chloroform from compounds of the type $RC(CCl_3){=}NH$ by potassium hydroxide [Houben and Fischer, *Ber.*, **66**, 339 (1933)] might be regarded as involving the removal of HX. (As suggested by a referee, however, CCl_3COOH might be hydrolyzed by NaOH to form $CHCl_3$ and NaOCOONa just as CBr_4 is hydrolyzed to form $CHBr_3$ and NaOBr.)

[7] Brady and Truszkowski, *J. Chem. Soc.*, **125**, 1087 (1924).

[8] Brady and Klein, *ibid.*, **127**, 844 (1925).