[Contribution from the Department of Chemistry of Iowa State College]

THE RELATIVE REACTIVITIES OF NORMAL BUTYL BROMIDE AND BROMOBENZENE TOWARD MAGNESIUM IN ETHER

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Several explanations have been proposed for the orienting influences of various elements and groups in substitution reactions of benzene and other aromatic types. The Flürscheim hypothesis has been criticized because of the implicit assumption that some bonds are strong and others weak. The following extract is from a recent text.[1] "Silver nitrate will remove bromine from methyl bromide much more readily than from bromobenzene, which appears to support Flürscheim's ideas, since it suggests that the strength of the bonds joining bromine to carbon is different in the two organic molecules. But in the formation of the Grignard reagent it is found that magnesium acts with *equal*[2] ease upon methyl bromide and bromobenzene; so that no difference in reactivity is noticeable."

Several studies in this Laboratory indicated that alkyl halides, in general, react more readily than the corresponding aryl halides with magnesium in ether to form the respective Grignard reagents. The results of the present studies support this view. First, in some semi-quantitative investigations on the effect of negative catalysts[3] on the formation of organomagnesium halides, it has been shown that *n*-butyl bromide reacts with magnesium in ether distinctly more readily than does bromobenzene to form the respective Grignard reagents.[4] Second, the yields of *n*-butylmagnesium bromide and phenylmagnesium bromide as quantitatively determined, under corresponding conditions, at several time intervals showed that larger amounts of the *alkyl*magnesium bromide were formed in a given time.

It should be remembered here that the reaction between an RX com-

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[1] "Recent Advances in Organic Chemistry" by Alfred W. Stewart, fifth edition, Vol. I, p. 338, 1927, published by Longmans, Green and Co., Ltd. The particular criticism in this and in other texts may possibly have its origin in Holleman's "Die direkte Einführung von Substituenten in den Benzolkern," p. 212–213, published by Veit and Co., Leipzig, in 1910. One of the statements made there is the following: "However, one observes that in ethereal solution the halogen in the benzene ring is just as easily replaced by magnesium as that in alkyl halides." No measurements of this were made (private communication from Dr. Holleman), but the observation is understandable in view of the comparative readiness with which bromobenzene reacts with magnesium in ether.

[2] The italics are ours.

[3] Studies by R. J. VanderWal.

[4] The color test described by Gilman and Schulze was used in these experiments, This Journal, 47, 2002 (1925), and *Bull. soc. chim.*, 41, 1279 (1927).

pound and magnesium to form a Grignard reagent is accompanied by other reactions, such as the Würtz-Fittig reaction which is probably preceded by the formation of free radicals and disproportionation.[5] Furthermore, the positive color test[4] for the Grignard reagent, despite its high sensitivity, must wait on the formation of an amount of the RMgX compound in excess of that required to react with any incidental moisture and impurities in the ether such as peroxides. Attention should be directed, in connection with these studies, to a recent paper by Rudd and Turner[6] on the competitive interaction of alkyl and aryl halides with magnesium. These authors allowed a mixture of two different halides (one mole of each) to compete for one atom of magnesium, and the product was analyzed for *halogen* after complete dissolution of the metal. Obviously their results do not represent the exact quantities of Grignard reagent formed, and there is the possibility that one RMgX compound may have affected the rate of formation of the other.[7] Both of these points were mentioned by them. The pairs of halides they allowed to compete for magnesium had *different* halogens.

Experimental Part

The quantitative experiments were made under the general conditions and in the special apparatus used by Gilman and co-authors in earlier studies on the quantitative estimation[8] of the Grignard reagent and on the yields[9] of some RMgX compounds.

The halides were very carefully dried and then distilled prior to use. Commercial magnesium was used and the particles (after crushing in a mortar and sieving) were essentially uniform. In each run 0.05 mole of halide, 0.054 atom of magnesium and 30 cc. of dry ether were used.

The magnesium was first covered with 6.5 cc. of ether and then, after having added a crystal of iodine, 30 drops (or its equivalent) of the halide was added and the mixture was heated for ten minutes without stirring in a bath kept at 45°. This insured the start of reaction prior to the addition of the main quantity of halide. The remainder of the halide and ether was then added rapidly with stirring (the time of addition here was ten seconds) and from this point was taken the time given in Table I.

At the end of a given time interval (forty-five or ninety seconds) the reaction flask

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[5] A preliminary account of this study was made at the St. Louis Meeting of the American Chemical Society, April 17, 1928, by Gilman, Fothergill, Kirby and Heck. The final results will be published shortly.

[6] Rudd and Turner, *J. Chem. Soc.*, **133**, 686 (1928).

[7] An indication of this is found in some competitive studies of halides, such as *n*-butyl bromide and bromobenzene, toward magnesium. The yields of derivatives of these two Grignard reagents (formed at the same time with an insufficient amount of magnesium) differ from the acid titration values.

[8] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923); Gilman and Meyers, *Rec. trav. chim.*, **45**, 314 (1926).

[9] Gilman and Meyers, THIS JOURNAL, **45**, 159 (1923); Gilman and McCracken, *ibid.*, **45**, 2462 (1923); *Rec. trav. chim.*, **46**, 463 (1927); Gilman and Zoellner, THIS JOURNAL, **50**, 425 (1928).

was chilled in a bath of ice and water. Experiments showed that the reaction was virtually stopped by such chilling, for the yield of RMgX at the beginning of the chilling period was only about 2.5% less than that determined at the end of one-half hour of chilling. Three aliquots were removed for analysis at the beginning of the chilling period. After removing the aliquots the mixture was allowed to react at room temperature for forty-five minutes and then two aliquots were removed for analysis.

The analyses of these final two aliquots have no essential bearing on the relative reactivities of the halides since the reaction was complete at that time.[9] However, they did serve, first, as an additional check on the technique and, second, to call attention to marked differences in the respective total quantities of Grignard reagents at the end of each experiment. For when runs were made with both halides, under the general conditions followed in the ninety seconds experiments but *without* removal of the three aliquots, the yield of phenylmagnesium bromide (92.7%) and that of *n*-butylmagnesium bromide (79.7%) checked those in the reactivity runs when interruptions were made for the removal of aliquots. Under the conditions usually employed for the preparation of the Grignard reagent (slow addition, etc.)[9] the yield of phenylmagnesium bromide is 96.2% and that of *n*-butylmagnesium bromide, 94%.[10] This marked drop in the yield of *n*-butylmagnesium as a consequence of rapid addition is of particular significance. It emphasizes a reactivity of *n*-butyl bromide that is distinctly greater than that shown by the respective quantities of Grignard reagent actually determined (see Table I) inasmuch as the drop in yield (from 94 to 79.7%) very probably resulted, in large part,[11] from *n*-butylmagnesium bromide being used up in side reactions.[5]

Table I includes the averages of several runs where aliquots were removed at two different time intervals. The aliquots from a given experiment agreed within the experimental error for such work, namely, about one per cent.[8,9] The average values for analyses made of duplicate runs of a given halide after ninety seconds of reaction agreed within 2.7%; and

TABLE I

RESULTS OF ANALYSES

Halide	Moles	Time of reaction, secs.	Yield of corresponding RMgX, %
Bromobenzene	0.05	45	36.9
n-Butyl bromide	.05	45	53.7
Bromobenzene	.05	90	51.7
n-Butyl bromide	.05	90	65.4

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[10] Other studies in progress on the effect of rapid addition of halide on the yield of Grignard reagent show no apparent correlation as yet with the type of RX compound used.

[11] In so far as the immediate purpose of this paper is concerned it does not matter how much of this drop is due to Grignard reagent that has disappeared as a result of side reactions. The significant thing is that the *n*-butyl bromide has reacted more rapidly than the bromobenzene toward magnesium.

those after forty-five seconds of reaction agreed within 6.5%. Quite probably these average errors can be significantly reduced with a more refined technique such as, for example, the use of a definite quantity of iodine instead of the somewhat arbitrary "crystal of iodine." The rates of some other halides are being measured under more exact conditions.

The authors wish to acknowledge help in some of these experiments from J. B. Dickey.

Summary

n-Butyl bromide reacts more rapidly than bromobenzene with magnesium in ether. This result is of direct value in connection with some theories proposed to account for orientation in the benzene nucleus.

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OXIDATION IN THE BENZENE SERIES BY GASEOUS OXYGEN. IV. MECHANISM OF THE SLOW OXIDATION OF SATURATED HYDROCARBONS

BY H. N. STEPHENS

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Previous papers by the writer[1] have shown that alkyl benzenes are oxidized slowly by gaseous oxygen at a temperature of about 100°. Methylbenzenes yielded mono-aldehydes and the corresponding acids, while hydrocarbons containing two or more carbon atoms in the side chain were attacked only at the α-carbon atom, yielding ketones. When alkyl substituents replaced all of the hydrogen on the α-carbon atom, no oxidation took place under the conditions employed; therefore we must conclude that the linkages between this particular carbon atom and its hydrogen are the points of weakness which are attacked by oxygen.

In studying some of these oxidations it was found that the water formed by the reactions exerted a retarding effect and later, when excess water was used with the hydrocarbons, complete inhibition of oxidation resulted. Important exceptions to this behavior were noted in hydrocarbons which have only one hydrogen atom attached to the α-carbon atom, in which cases no inhibitory action was noted.

In seeking an explanation of the inhibitory action of water, it did not seem to us sufficient merely to classify it under the vague and unsatisfactory term "anticatalysis." Neither did it seem possible to account for the phenomenon on the basis of a protective action in which the water molecules might be assumed to attach themselves loosely to the hydrocarbon molecules, preventing ready access of oxygen to the vulnerable

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[1] Stephens, THIS JOURNAL, **48**, 1824, 2920 (1926).