an excellent yield of benzylmagnesium chloride (see following paper); whereas if allyl bromide is added at once to magnesium in ether, very little allylmagnesium bromide results, and most of the allyl bromide couples to form diallyl. However, by the special conditions described recently by Gilman and McGlumphy[12] it is possible to obtain allylmagnesium bromide in greater than 90% yields.

The Naphthylmagnesium Bromides.—The yield of α-naphthylmagnesium bromide reported earlier[2b] is incorrect. This was very probably due to the sparing solubility of this Grignard reagent in ether (see footnote *h* to Table I). The comparatively high yield of β-naphthylmagnesium bromide is both interesting and valuable in view of the discouragingly low yields of this RMgBr compound reported by others.[13]

The authors gratefully acknowledge assistance from R. W. Borgeson and L. L. Heck.

Summary

The yields of a number of typical Grignard reagents have been determined. Where comparisons can be made with earlier determinations these revised yields are higher. Attention is directed to a number of generalizations, particularly the apparent alternation in yields with the *n*-alkyl bromides.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE EFFECT OF RAPID ADDITION OF HALIDE ON THE YIELDS OF SOME GRIGNARD REAGENTS

BY HENRY GILMAN, E. A. ZOELLNER AND J. B. DICKEY

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Introduction

In studies on the relative reactivities of alkyl and aryl halides toward magnesium in ether,[1] all of the halide is added at once to the magnesium in ether and the reaction is interrupted at regular intervals to determine the rate of reaction. This makes it necessary to have comparative values showing the yields of Grignard reagent when all of the halide is added at once. Yields under such conditions have been determined and are here reported. The results of such studies have an importance over and above

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[12] Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

[13] Loevenich and Loesser, *Ber.*, **60**, 320 (1927), reported a 28.5% yield of β,β'-dinaphthyl and no β-naphthoic acid when their reaction product of β-bromonaphthalene and magnesium was treated with carbon dioxide. Probably the highest yield of a compound from β-naphthylmagnesium bromide is a 50% yield of β-naphthaldehyde reported by Chichibabin, *Ber.*, **44**, 443 (1911).

[1] A preliminary account of these studies has been reported by Gilman and Zoellner, THIS JOURNAL, **50**, 2520 (1928).

their value for rate studies. These considerations are treated in the Discussion of Results.

Experimental Part

The general design of the apparatus,[2] the quantities of reagents, the starting of the reaction, the rate of stirring, the conclusion of the reaction and the method of titration were identical with the procedure described in the preceding paper by Gilman, Zoellner and Dickey.[3] The reaction was started with 20 drops (about 0.2 cc.) of halide in 6.5 cc. of ether and a crystal of iodine weighing about 0.04 g.

Then 23.5 cc. of ether was added to the remainder of the halide contained in the dropping funnel. The stirrer was started and kept at a rate of about 750 r. p. m., and the halide and ether were added as rapidly as possible. The time of addition was about ten seconds.[4] All reactions were allowed to continue at room temperature and from time to time stirring was interrupted to ascertain evidence of any reaction. When the reaction was apparently concluded, the mixture was treated in the manner described in the preceding paper.

Approximate times were noted when there was no evidence of reaction subsequent to the rapid addition of all of the halide. For the alkyl halides[5] and benzyl chloride this time was nine to twelve minutes; for bromobenzene it was about twelve to fifteen minutes; and for the other aryl halides the time was about one hour.

The average yields with rapid addition given in Table I are of at least two independent runs. The widest variation between any pair of runs was 2.5%. Each run in turn is an average based on at least two aliquots which agreed between 0.7% and 1.5%.[3] For purposes of comparison, Table I also includes the average percentage yield under optimal conditions and the difference between these two yields, namely, the average percentage *drop* in yield with rapid addition of halide.

Discussion of Results

A glance at Table I shows that there is a drop in yield with each of the compounds studied when the halide is added rapidly. This might have been predicted in view of the results obtained by Gilman and Meyers[6] in their study of the optimal conditions for the preparation of ethylmagnesium iodide. They showed that the yield of ethylmagnesium iodide was 93.3% when the ethyl iodide was added over a forty-five minute period and 85.2% when the ethyl iodide was added as rapidly as possible, which was about thirty seconds under the conditions of those experiments. With this result as a basis, all later investigations in this Laboratory[7] on optimal conditions for other Grignard reagents incorporated, among other factors, a slow rate of addition.

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[2] The bore of the graduated neck of the reaction flask was 20 mm. instead of 15 mm. This greater width was necessary in order to reduce the accumulation of reaction mixture in the neck of the flask as a consequence of the vigorous reaction attendant on the rapid addition of halide.

[3] Gilman, Zoellner and Dickey, This Journal, **51**, 1576 (1929).

[4] In the earlier study by Gilman and Meyers, *ibid.*, **45**, 159 (1923), the time for the rapid addition of ethyl iodide was about thirty seconds.

[5] See preceding paper for the slow reaction with *n*-butyl chloride.

[6] Gilman and Meyers, This Journal, **45**, 159 (1923).

[7] Literature references to these articles are given in footnotes 2b, 2c, 11 and 12 of the preceding paper (ref. 3); see also footnote *d* to Table I of this paper.

TABLE I

AVERAGE PERCENTAGE YIELDS OF RMgX COMPOUNDS AFTER RAPID ADDITION OF HALIDE, AND DECREASE IN YIELDS FROM NORMAL ADDITION

Halide Used	Yield, opt. cond. %	Yield, hal. added rapidly, %	Diff. or drop in yield, %	Halide Used	Yield, opt. cond. %	Yield, hal. added rapidly, %	Diff. or drop in yield, %
Ethyl bromide	93.1	86.6	6.5	*n*-Heptyl bromide	88.8	72.9	15.9
n-Propyl bromide	91.7	82.5	9.2	*n*-Octyl bromide	88.4	73.3	15.1
*Iso*propyl bromide	84.0	70.5	13.5	*n*-Butyl chloride	91.2	90.6	0.6
n-Butyl bromide	94.0	79.2	14.8	*n*-Butyl iodide	85.6	67.8	17.8
*Iso*butyl bromide[a]	87.2	76.7	10.5	Benzyl chloride	93.2	92.9	0.3
Sec.-butyl bromide[b]	77.7	61.6	16.1	Bromobenzene	94.7	89.8	4.9
Tert.-butyl bromide[c]	25.1	17.8	7.3	*o*-Bromotoluene	92.7	88.3	4.4
n-Amyl bromide	88.6	73.2	15.4	*m*-Bromotoluene	88.0	81.3	6.7
Iso-amyl bromide	88.0	70.2	17.8	*p*-Bromotoluene	86.9	83.3	3.6
Sec.-amyl bromide[b]	66.8	49.2	17.6				
Tert.-amyl bromide	23.7	19.1	4.6	α-Bromonaphthalene	94.8	91.7	3.1
n-Hexyl bromide	92.0	77.2	14.8				
				β-Bromonaphthalene[d]	83.8	81.3	2.5

[a] The 10.5% drop in yield is the average of three independent runs. The third, which agreed closely with the other two, was made because it is difficult to understand why the drop in yield with *iso*butyl bromide should be less than the drop with *n*-butyl bromide and *iso*-amyl bromide.

[b] Three independent runs were made with *sec.*-butyl and *sec.*-amyl bromides in order to note any possible irregularity with these halides.[3] The several runs gave good checks.

[c] Three independent runs were made with *tert.*-butylmagnesium bromide and all checked within 0.6%.

[d] A greater drop in yield was expected with β-naphthylmagnesium bromide because Loevenich and Loesser, *Ber.*, **60**, 320 (1927), reported a 28.5% yield of β,β'-dinaphthyl and no β-naphthoic acid when their reaction product of β-bromonaphthalene and magnesium was treated with carbon dioxide (see ref. 13 of ref. 3.)

However, the extent of the drop in yield could not have been predicted with any exactitude in several of the compounds studied. First, benzylmagnesium chloride shows practically no drop in yield with rapid addition. This is astonishing in view of the statements in the literature that unless special precautions are taken in the preparation of this Grignard reagent the yield of coupling product (in this case, dibenzyl) can reach 30%. Second, the drop in yield with *tert.*-butyl- and *tert.*-amylmagnesium chlorides is less than one might have expected in view of the studies by Gilman and Zoellner[8] on the optimal conditions for the preparation of these *tertiary* Grignard reagents. They found it necessary to add the tertiary halides extremely slowly (about two to three hours) in order to get a good yield of the RMgCl compound. However, consideration should be given to the fact that there is already a very marked drop in yield from the very special conditions of Gilman and Zoellner[8] for the two tertiary chlorides, and the

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[8] Gilman and Zoellner, THIS JOURNAL, **50**, 425 (1928); *Rec. trav. chim.*, **47**, 1058 (1928).

more general conditions of Gilman, Zoellner and Dickey[3] for *all* types of Grignard reagents. In the former case the yield was 58%[9] in a two-hour period of addition and in the latter case about 25% in a 30 to 35 minute period of addition.

In general the alkyl halides show a greater drop in yield on rapid addition than do the aryl halides. With the alkyl halides the iodide shows a greater drop than the bromide and the bromide, in turn, shows a greater drop than the chloride. With an R group of a given weight, the branched-chain isomers show a greater drop than the *normal* or straight-chain compound.[10]

The greater drop of the alkyl halides over the aryl halides makes an explanation based on the greater activity of the halogen in alkyl halides very attractive. However, over and against any rigid interpretation on this basis is the almost insignificant drop with benzyl chloride, a halide that contains halogen that is comparatively highly reactive.[11] Quite probably a correlation will be found on the basis of some studies now in progress on the preliminary formation of free radicals in the preparation of organometallic compounds.[12]

The results obtained in this study have a practical value for synthetic purposes. For example, benzylmagnesium chloride can be prepared in excellent yield by the rapid addition of halide, and a reasonably rapid rate of addition can be used for the preparation of the *aryl*magnesium halides investigated without serious impairment in yield. The results also emphasize the necessity of special methods for the preparation in optimum yields of different types of RMgX compounds.

It is interesting to note, particularly from a preparative viewpoint, that in a *rapid* addition of halide there is little to be gained in having the reaction start with a small part of the halide prior to the rapid addition of practically all of the halide. With all the experiments reported in Table I the reaction was started with 20 drops of the halide and a crystal of iodine. In other experiments with several typical halides (*n*-butyl bromide, benzyl chloride and bromobenzene) it was observed that the yield was only about 1% lower than those reported when *all* of the halide was added at once (with or without the addition of a crystal of iodine).

[9] The yield of *tert.*-butylmagnesium chloride is appreciably higher (at least 69.5%) in larger sized runs (about 2.5 moles).[8]

[10] We have no explanation at present for the lesser drop of *iso*butylmagnesium chloride (10%) when compared with that of *iso*-amylmagnesium chloride (17.8%); see footnote *a* of Table I.

[11] We should again like to direct attention to the fact that the rapid addition of allyl bromide to magnesium in ether gives little allylmagnesium bromide. However, Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928), have shown that this Grignard reagent can be obtained in yields greater than 90% by the slow addition of allyl bromide to an excess of finely-divided magnesium.

[12] Gilman and Fothergill, THIS JOURNAL, **50**, 3334 (1928); also Gilman and Kirby, *ibid.*, **51**, 1571 (1929).

Summary

A study has been made of the drop in yield of Grignard reagents when the halide is added very rapidly to magnesium in ether and some generalizations have been drawn from these results.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

THE CONSTITUTION OF BANDROWSKI'S BASE

BY JOHN J. RITTER AND GUNTHER H. SCHMITZ

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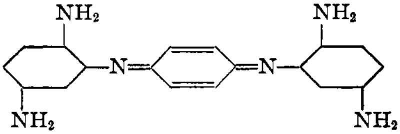
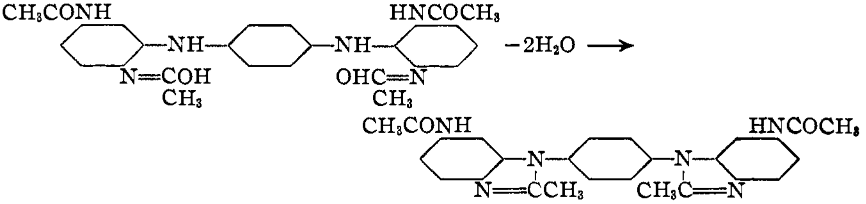
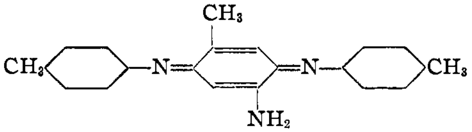
Introduction

Bandrowski[1] obtained, on ferricyanide oxidation of *p*-phenylenediamine in aqueous ammoniacal solution, a product to which he assigned the structure shown. This constitution is based on elementary analysis, molecular weight determination, production of *p*-phenylenediamine on zinc-dust distillation, the formation of a tetra-acetyl derivative, and ring-closure with the formation of a dipyrazole on reduction of the tetra-acetyl derivative, as follows





In view of the fact that *p*-toluidine has been shown by Barsilowski[2] and Green[3] to yield on oxidation a base of the formula (A), it appears quite

A 

possible that *p*-phenylenediamine might behave similarly, to yield the following isomer (B) of the Bandrowski base. Its properties, as observed

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[1] Bandrowski, *Monatsh.*, **10**, 123 (1889); *Ber.*, **27**, 480 (1894).

[2] Barsilowski, *ibid.*, **6**, 1209 (1873); *ibid.*, **8**, 695 (1875).

[3] Green, *ibid.*, **26**, 2772 (1893).