

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

**THE EFFECTS OF ACTIVATED AND NON-ACTIVATED
MAGNESIUM-COPPER ALLOY ON THE YIELDS OF
SOME ORGANOMAGNESIUM HALIDES**

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Introduction

Activated magnesium-copper alloys containing 12.75¹ and 14.5%² of copper are apparently the best known catalysts for initiating reactions between RX compounds and magnesium in ether.³ It has always been recommended that a small quantity of the catalyst be used to start the reaction, and that subsequently the reaction with the major part of the RX compound be carried out with ordinary magnesium. However, in studies on the preparation of the di-Grignard reagent from *p*-dibromobenzene,⁴ it was observed that the highest yield of terephthalic acid (obtained subsequent to carbonation) resulted when a large excess of the activated alloy was used. This and the peculiar effects of the activated alloy and of varying quantities of iodine on the preparation and the yields of phenylmagnesium chloride⁵ and other RMgX compounds was the basis for the statement: "Related unusual results with other RX compounds using varying quantities of iodine and alloy will be reported later."⁶ We are now reporting some of these results from an as yet uncompleted study. The following paper on the capture of free radicals describes some additional experiments⁵ concerned with the effects of an excess of iodine on the yields of some RMgX compounds.

The results here reported indicate that an equivalent of the alloy, either as such or after activation with iodine, decreases the yields of some typical Grignard reagents. The decrease is generally greater with the activated alloy. However, an excess of either the activated or non-activated alloy appears to increase the yield in some cases to those values obtainable when ordinary magnesium turnings or powder is used. For all practical purposes these variations in yield with the use of the alloy are without essential significance because only a very small quantity (usually 0.2 g.) of the activated alloy is used to initiate the reaction. This is established by experiments in which 0.19 to 0.51 g. of activated 12.75% alloy was used at first, the reaction with RX compound being

¹ Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1928).

² Gilman and Heck, *Bull. soc. chim.*, **45**, 250 (1929).

³ References to some of the applications by others of the activated alloy are: Hurd and Webb, *This Journal*, **49**, 546 (1927); Shepard, Winslow and Johnson, *ibid.*, **52**, 2089 (1930).

⁴ Gilman, Beaber and Jones, *Rec. trav. chim.*, **48**, 597 (1929).

⁵ Gilman and St. John, *ibid.*, **49**, 717 (1930).

then completed with 1.1 atoms of ordinary magnesium turnings. With 0.19 g. of the activated alloy and *n*-butyl bromide the yield was 1–4% below normal, and the drop increased to 7% when 0.51 g. of activated alloy was used; with 0.25 g. of activated alloy and benzyl chloride, the yield was decreased 0–3%; and with 0.19 or 0.48 g. of activated alloy and bromobenzene the yield was unaffected.

The depression of the yield is probably not due to a reaction between the alloy and RMgX compound already formed, because in one experiment 1.5 g. of the 12.75% alloy when refluxed for ten minutes with preformed *n*-butylmagnesium bromide did not lower the yield within experimental error. The drop in yield when more than the recommended quantity of activated alloy is used may be due in part to the iodine or magnesium iodide contained therein, because the following paper shows that iodine or magnesium iodide when used in more than a very small amount or less than a full equivalent also lowers the yield of some Grignard reagents. It appears that a very small, and yet effective, quantity of either iodine or the activated alloy is without essential effect on the yield.

Experimental Part

The apparatus and general technique was that used in related studies.⁶ The powdered alloy, as such or activated, was covered with 5 cc. of ether; then 20 drops of the pure RX compound and a crystal of iodine (always used with the non-activated alloy) was added. The mixture was heated for ten minutes by means of a water-bath at 45°. Then the remainder of the halide (a total of 0.05 mole) mixed with 25 cc. of ether, was added over a period of thirty minutes with stirring. After all of the halide had been added, the reaction mixture was stirred for an additional ten minutes.

TABLE I
YIELDS OF RMgX COMPOUNDS FROM UNACTIVATED AND ACTIVATED ALLOYS

Halide (0.5 mole)	G. ^a	Unactivated alloy % Yield, RMgX ^b	Activated alloy G. ^c	% Yield, RMgX ^b	Ordinary Mg turnings, % Yield RMgX ^d
<i>n</i> -C ₄ H ₉ Br	1.5	55.4, 55.8 (63.1) ^e	2	62.8	94
<i>n</i> -C ₄ H ₉ Br			3	67.9	
<i>n</i> -C ₄ H ₉ Br			5	80	
C ₆ H ₅ CH ₂ Cl	1.5	74.8 (83) ^e			93.1
C ₆ H ₅ CH ₂ Cl	2.0	89.5 ^f	2	72.6	
C ₆ H ₅ Br	1.5	82.3, 83.9, 83.7 (88.8) ^e	2	79	94.7 ^d
C ₆ H ₅ Br	2.0	94	3	97.8	
C ₆ H ₅ Br			5	98.7	
<i>p</i> -CH ₃ C ₆ H ₄ Br	1.5	87.8			86.9
<i>p</i> -CH ₃ C ₆ H ₄ Br	2.0	92	2	78.8	

^a One equivalent or 0.05 mole of the alloy is 1.38 g.

^b Each percentage yield listed is an average of at least two analyses made from one preparation.

⁶ Gilman, Zoellner and Dickey, *THIS JOURNAL*, 51, 1576 (1929).

^c The alloy used here was *re*-activated. In a few experiments carried out with activated alloy which was exposed to a somewhat humid atmosphere for twenty-five minutes after activation and then used directly without re-activation, the yields of *n*-butylmagnesium bromide from 2.0 g. of such alloy were 43.9 and 45%, and bromobenzene did not react. One equivalent of the activated alloy is 1.67 g.

^d These percentages are taken from the studies described in Ref. 6, wherein ordinary magnesium *turnings* were used. They are, therefore, not comparable with the results obtained with the powdered alloy. This finds support in an experiment carried out during the present studies where the yield of phenylmagnesium bromide prepared from 1.33 g. of 100-mesh ordinary magnesium was 97.3%. See, also, Gilman and Fothergill, *Iowa State Coll. J. of Sci.*, 4, 351 (1930), for the effect of an excess of fine magnesium on the yields of some Grignard reagents. The smaller drop in yield with an excess of the alloy may be due, in part, to the essential presence of an excess of fine magnesium.

^e The percentages in parentheses are those obtained with the 12.75% copper-magnesium alloy of 30–80 mesh. In all other cases the alloy used contained 11.25% copper, and was of 60–200 mesh.

^f With 6 g. of 12.75% copper-magnesium alloy of 30–80 mesh the yield of benzylmagnesium chloride was practically equal to that obtained with turnings of ordinary magnesium.

Summary

When equivalent quantities of copper-magnesium alloy are used alone, either in the activated or non-activated condition, the yields of some Grignard reagents are lowered. However, small, but effective, quantities of the activated alloy appear to have no significant effect on the yield. The other more commonly used catalyst, iodine, apparently has the same general effect as the alloy on the yields of some Grignard reagents (see following paper).

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THE PREPARATION OF ORGANOMAGNESIUM HALIDES IN THE PRESENCE OF MAGNESIUM IODIDE. STUDIES ON THE CAPTURE OF FREE RADICALS

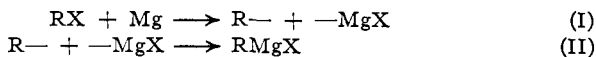
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Introduction

One of the current interpretations of the preparation of Grignard reagents involves the prior or intermediate formation of free radicals, after the following representation.



There are several kinds of evidence for the intermediate formation of free radicals (R·) in accordance with Reaction I. The side reactions that invariably accompany the preparation of RMgX compounds, from RX compounds and magnesium, are best explained by the coupling, dispropo-