

^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

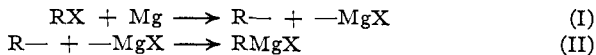
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Introduction

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-

portionation and rearrangement reactions of the free radicals.¹ Furthermore, there is direct experimental evidence in support of Reaction II, inasmuch as it has been shown² that triarylmethyls, like $(C_6H_5)_3C-$, will combine with the hypothetical $-MgX$ or its equivalent (the binary system, $Mg + MgX_2$, of Gomberg) to give triphenylmethylmagnesium halide, $(C_6H_5)_3CMgX$.

However, because triarylmethyls are, in a sense, a special class of free radicals, it was felt that a more complete case for Reaction II would be had if another type of free radical, as yet not isolated, were captured incidental to the formation of $RMgX$ compounds. For this purpose, a study was first made of the reaction between *tert.*-butyl chloride and magnesium in ether. Under ordinary conditions it is very difficult to get a satisfactory yield of *tert.*-butylmagnesium chloride³ because of the marked tendency of the hypothetical intermediate *tert.*-butyl radicals to undergo coupling and, particularly, disproportionation to isobutane and isobutylene.

One way of capturing the *tert.*-butyl radicals is to have present, during the reaction between *tert.*-butyl chloride and magnesium, the $-MgX$ (or the binary system, $Mg + MgX_2$). A procedure of this kind was successful in contributing to the improvement of the yield of triphenylmethylmagnesium chloride;⁴ and, as already stated,² the independent systems, $R-$ and $-MgX$, have been combined to give triphenylmethylmagnesium halides. When, however, this principle was employed in the preparation of *tert.*-butylmagnesium chloride we either did not capture the intermediate *tert.*-butyl radical, or having captured it we did not hold it for long because the yields of *tert.*-butylmagnesium chloride were, in general, actually reduced. In short, the binary system ($Mg + MgI_2$) did not make it possible to obtain a yield of *tert.*-butylmagnesium halide in excess of that obtained under optimal conditions when none of the binary system was purposefully added; but a trace of iodine (or of MgI_2 or $(Mg + MgI_2)$) or a full equivalent of the binary system did give a yield equal to that obtained when no magnesium iodide was added, and intermediate quantities depressed the yield—the greatest lowering being observed with about 0.25 equivalent of the binary system per equivalent of RX compound. This depression of yield very probably occurs in the early stages of the formation of the $RMgX$ compound, inasmuch as magnesium or magnesium iodide or a combination of the two is without essential effect on the *tert.*-butylmagnesium chloride after it is once formed. Apparently the same sort of a depression, but to a less marked extent,

¹ A recent study with leading literature references is Gilman and St. John, *THIS JOURNAL*, **52**, 5017 (1930).

² Gilman and Fothergill, *ibid.*, **51**, 3152 (1929); Gomberg and Bachmann, *ibid.*, **52**, 2455 (1930); Bachmann, *ibid.*, **52**, 3287, 4412 (1930).

³ Gilman and Zoellner, *ibid.*, **50**, 425 (1928); *Rec. trav. chim.*, **47**, 1058 (1928).

⁴ Gilman and Zoellner, *THIS JOURNAL*, **51**, 3493 (1929).

occurs with *n*-butylmagnesium bromide. It would be unwise to generalize from these two illustrations because of the frequently observed distinct differences between apparently related organomagnesium halides.

From the preliminary report now made, it follows that the generally used catalyst (iodine) has a deleterious effect on the yield unless used in very small quantities or in very large quantities. A like phenomenon is reported in the preceding paper,⁵ when another more recent catalyst, the activated magnesium-copper alloys, is used. Fortunately, these effects are of no apparent serious moment from a practical viewpoint because the catalysts are almost always used in very small quantities merely to initiate reaction between a part of the RX compound and magnesium. In this connection it is interesting to recall that the time required to prepare phenylmagnesium chloride in ether solution decreases in a regular manner with the increase of iodine.⁶

Experimental Part

The apparatus and general technique was that used in related studies.⁷ In the *n*-butylmagnesium bromide experiments the 30-80 mesh magnesium was first covered with 16 cc. of ether; then the selected quantity of iodine was added; when the iodine color disappeared, 20 drops of the *n*-butyl bromide was added directly without a solvent; the mixture was then refluxed for ten minutes; and, finally, the remainder of the halide (totaling 0.05 mole) in 21 cc. of ether was added with stirring at a uniform rate over one hour.

A variation of this procedure was used with the *tert.*-butylmagnesium chloride experiments. Because preliminary experiments showed that erratic results generally followed the addition of the chloride to the magnesium and magnesium iodide in ether, a part of the selected quantity of iodine was added subsequent to the formation of the major portion of magnesium iodide and subsequent to the addition of 20 drops of the chloride. In this manner the reaction between the *tert.*-butyl chloride and magnesium set in smoothly and there was no difficulty in getting concordant results. With each halide the quantity of fine magnesium used was one atom equivalent for each atom equivalent of iodine, in addition to one atom per mole of *n*-butyl bromide and three atoms per mole of *tert.*-butyl chloride.

The results of the experiments are contained in Table I. The average values are those of at least two preparations from each of which at least two aliquots were removed for titration. The agreements were of an uncommonly high order when one considers the great sensitivity of an RMgX compound like *tert.*-butylmagnesium chloride.

⁵ Gilman and Zoellner, *THIS JOURNAL*, **53**, 1581 (1931).

⁶ Gilman and St. John, *Rec. trav. chim.*, **49**, 717 (1930).

⁷ Gilman, Zoellner and Dickey, *THIS JOURNAL*, **51**, 1576 (1929).

A like degree of duplicability of results with *tert.*-butylmagnesium iodide prepared in the presence of magnesium iodide was not observed in a few preliminary experiments. Here the yields of RMgI compound in two independent preparations using 0.08 g. or 0.0125 atom equivalent of iodine were 57.0 and 52.3%; and with 6.35 g. or 1.0 atom equivalent of iodine, the yields were 55.1 and 58.4%. These experiments with the iodide were carried out because of the possibility of magnesium iodide reacting with *tert.*-butyl chloride or *tert.*-butylmagnesium chloride to give *tert.*-butylmagnesium iodide.

TABLE I
EFFECT OF IODINE ON YIELD OF *n*-BUTYLMAGNESIUM BROMIDE AND *Tert.*-BUTYL-
MAGNESIUM CHLORIDE

Iodine		Av. % yield of <i>n</i> -C ₄ H ₉ MgBr	Av. % yield of (CH ₃) ₃ CMgCl
G.	Atom equivalent		
None	None	95.9 ^a	83.3
0.08	0.0125	96.5 ^a	83.6
.16	.025	..	77.1
.32	.05	95.6	72.2
.64	.1	93.5	65.5 ^b
1.28	.2	92.6	64.9
1.90	.3 ^c	96.0	64.8
2.54	.4	94.9	71.8
3.81	.6	95.1	76.2
6.35	1.0	96.4	79.7

^a With 0.04 g. or 0.0063 equivalent of iodine the yield was 99%. This unusually high value was checked. Further work is in progress on the effect of very small quantities of iodine on the yields of some other RMgX compounds.

^b The low yield by titration was confirmed in a carbonation experiment with this relative quantity of iodine and with the 0.08 g. of iodine experiment which gave the 83.6% of Grignard reagent. It is interesting to note that this very high yield of RMgCl makes it possible to obtain trimethylacetic acid from it by carbonation in a 75% yield.

^c In the experiments using 0.3 or more atom equivalent of iodine, it was necessary to cover the magnesium with 35 cc. and not 16 cc. of ether. This, however, is without apparent effect on the relative yields because there was no change in yield when some of the preparations using less than 0.3 atom equivalent of iodine were carried out with 35 cc. instead of 16 cc. of ether.

Summary

In studies concerned with the capture of free radicals formed during the preparation of organomagnesium halides it has been shown that the quantity of iodine used to catalyze the formation of *tert.*-butylmagnesium chloride has a significant effect on the yield. There is no appreciable lowering of yield with a very small amount or a full atom equivalent of iodine. Another catalyst, the magnesium-copper alloy which is used with more refractory RX compounds, also appears to have a corresponding effect on the yields of other RMgX compounds.