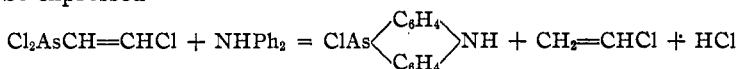


were led to compare the analogous reaction using  $\beta$ -chlorovinylchloro-arsine as described by Lewis and Stiegler [THIS JOURNAL, 47, 2546 (1925)]. They found (*loc. cit.*, p. 466) that not only is 10-chloro-5,10-dihydrophenarsazine and not "6-chlorovinylphenarsazine" formed by the action of  $\beta$ -chlorovinylchloro-arsine on diphenylamine, but, by proving the production of vinyl chloride in the reaction, showed that the course of the latter may be expressed



Burton and Gibson also proved that the reaction between phenyldichloro-arsine and other substituted diphenylamines and of  $\beta$ -chlorovinylchloro-arsine and phenyl- $\alpha$ -naphthylamine proceeds analogously. These results have since then been fully verified by Seide and Gorski [*Ber.*, 62, 2186 (1929)]. Scherlin and Epstein [*Ber.*, 61, 1823 (1928)] have also shown that the reaction between  $\beta$ -chloro-ethylchloro-arsine and diphenylamine yields 10-chloro-5,10-dihydrophenarsazine, the reaction being quite similar.

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**Phenylmagnesium Fluoride.**—The relative reactivities of RX compounds with magnesium in ether is in the order RI > RBr > RCl > RF. Actually, only one RMgF compound (*n*-amylmagnesium fluoride) has been prepared, and this synthesis was effected by unusually extensive refluxing with a large quantity of iodine.

In connection with studies concerned with improved catalysts for the formation of organomagnesium halides, it was observed that none of the highly active catalysts induced a reaction between fluorobenzene and magnesium in ether. There has been described recently a satisfactory method for the preparation of phenylmagnesium chloride in the absence of a solvent, and this method is distinctly superior to the very slow formation of this compound when ether is used with varying quantities of iodine and with the magnesium-copper alloy.<sup>1</sup> In this study involving no solvent and a sealed tube it was shown that when fluorobenzene was heated with magnesium at 300° for about 200 hours, a small quantity of diphenyl formed. The formation of diphenyl is almost certain evidence for the intermediate formation of phenylmagnesium fluoride,<sup>2</sup> and the statement was made that this Grignard reagent would probably be prepared by heating at a lower (as yet undetermined) temperature for a longer time.

<sup>1</sup> Gilman and St. John, *Rec. trav. chim.*, 49, 717-723 (1930).

<sup>2</sup> Gilman and Brown, THIS JOURNAL, 52, 5045 (1930).

It now appears, in strict accordance with our knowledge of the very deliberate rate of reaction of chlorobenzene and magnesium in ether,<sup>1</sup> that even the most refractory RX compound will probably react with magnesium in ether if sufficient time be permitted for such a reaction. This finds support in some studies made in sealed, small test-tubes wherein it has been shown that fluorobenzene undergoes reaction with the activated magnesium-copper alloy in ether after being allowed to stand at room temperatures for eighteen months, and that phenylmagnesium fluoride is formed. Individual tubes opened at intervals of one month showed no positive color test at the end of six months. Reaction, therefore, had set in some time between six and eighteen months. Quite probably a compound like *p*-difluorobenzene will form *p*-fluorophenylmagnesium fluoride more readily, because *p*-dichlorobenzene reacts more readily than chlorobenzene.

It is altogether reasonable to expect that a distinctly shorter time will be required for the formation of phenylmagnesium fluoride when the proper temperature range in sealed-tube experiments is determined or when superior catalysts are discovered. At present, however, if one desires a *pure* RMgX compound from a highly inert RX compound, it is merely necessary to enclose the reactants in a container to exclude the atmosphere and moisture and wait for the reaction to run its course. The compensations for such devastating delays are that the RMgX compound will almost certainly be of a high order of purity and will be formed in a high yield because side reactions are drastically reduced with the use of relatively inert RX compounds. The difficulties in most cases are more apparent than real because of the ready accessibility of the related RBr and RI compounds. In our case we needed phenylmagnesium fluoride in studies on the relative reactivities of some organometallic compounds.

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**A New Compound of Benzaldehyde and Anthrahydroquinone.**—During an investigation on the autoxidation of anthrahydroquinone in benzaldehyde solution,<sup>1</sup> it was found that such a solution (oxygen being excluded), when containing a trace of hydrochloric acid, gave on standing in the dark at room temperature for twelve to seventy-two hours a new compound in good yield. The presence of benzoic acid appeared to favor larger yields. No reaction occurred: (1) in the absence of hydrochloric acid; (2) with anthrone substituted for anthrahydroquinone; or (3) between anthrahydroquinone and either benzoic acid or benzoin in acetone solutions.

<sup>1</sup> Bäckström and Beatty, to be published.