mercuri-2-nitroanisole and heated for a few minutes. On cooling, some of the slightly soluble nitrate derivative was obtained.

Acetoxymercuri-*m*-cresol.—Five grams of *m*-cresol in 5 cc. of acetic acid was heated for one hour with 5 g. of mercuric acetate in 5 cc. of acetic acid, adding enough water to just maintain a clear solution (about 9 or 10 cc.). After standing for twenty-four hours, crystals precipitated, and on recrystallizing from alcohol with a trace of acetic acid, they melted at 177°. On standing for an additional twenty-four hours, the mother liquor precipitated more crystals which, after recrystallization, melted at 155°. This corresponded to 4-acetoxymercuri-*m*-cresol described by Mameli and Piaggesi.[9] A mixed melting point with the 177° compound was depressed. None of the 6-acetoxymercuri derivative melting at 130° was obtained.

To determine the position of the mercury in the compound melting at 177°, a small amount of it was treated with more mercuric acetate in acetic acid solution. On purifying the product obtained, it melted with decomposition at 235°. This was the decomposition temperature reported by Mameli and Piaggesi[9] for the 2,4-diacetoxymercuri-*m*-cresol derivative of 4-acetoxymercuri-*m*-cresol melting at 155°. Since both gave the same diacetoxymercuri derivative, it follows that the compound melting at 177° is 2-acetoxymercuri-*m*-cresol.

Tolylmercuric Lactate.—Tolylmercuric chloride, made from the acetate and sodium chloride, was refluxed in alcoholic solution for one hour with an excess of moist silver oxide. After filtering from the insoluble material and concentrating to a small volume, a slight excess of lactic acid was added to the warm solution. On setting aside to cool, tolylmercuric lactate crystallized. It was recrystallized from alcohol and dissolved in water for bacteriological examination.

Summary

A number of different types of aromatic mercury derivatives in which mercury is attached to carbon have been prepared and studied.

The mercury derivatives of more complex structure were not as effective as bacteriostatic agents as the mercury derivatives of hydrocarbons or phenols with limited substituents.

Orthohydroxyphenylmercuric chloride was found to be the most powerful bacteriostatic agent of the mercury derivatives studied.

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(9) Mameli and Piaggesi, *Gazz., chim. ital.*, **62**, 158 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

Relative Rates of Formation of Some Organomagnesium and Organolithium Compounds

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

It has been demonstrated that *n*-butylmagnesium bromide forms more rapidly than phenylmagnesium bromide;[1] and that the order of decreasing activity of *n*-butyl halides with lithium is C_4H_9I, C_4H_9Br, C_4H_9Cl.[2] The rate studies with lithium were carried out by Ziegler and Colonius[2] incidental to their classical investigation on the preparation of organolithium compounds. Inasmuch as the yields of some organolithium compounds have been improved and also because it has been shown that many organolithium compounds can be prepard as conveniently as the related Grignard reagents it seemed advisable to compare the relative rates of formation of some of these two organometallic types under corresponding conditions. A discussion of the results follows the Experimental Part.

Experimental Part

The procedure was essentially that used in the earlier study with *n*-butyl- and phenylmagnesium bromides.[1] One refinement was in the reduction of time (from seventeen to one or two seconds) to arrest reaction after the designated periods during which the halides reacted with the magnesium in ether. In the shortened interval of one or two seconds the reaction mixture was cooled internally by the addition of cold, dry ether, and cooled externally by the application of an ice–salt bath; and the rate of stirring increased from 380–390 to 2000–2200 r.p.m. After detaching the special flask, aliquots were removed immediately for analysis by the acid titration method. The values given in the tables are averages of numerous experiments each of which, in turn, is an average of two or more aliquots. There was the usual agreement in results for work of this kind, details for which have been supplied in earlier papers. All values given in the tables have been corrected for "drop conditions" or the rapid addition of RX compound.

In some preliminary experiments the rates of formation of *n*-butylmagnesium chloride and phenylmagnesium bromide were determined, with stirring at 1000 and 380–390 r. p. m., respectively. These results are given in Table I.

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(1) Gilman and Zoellner, THIS JOURNAL, **50**, 2520 (1928). See also, Rudd and Turner, *J. Chem. Soc.*, 686 (1928), for a study of the competitive reactions of RX compounds for magnesium.

(2) Ziegler and Colonius, *Ann.*, **479**, 135 (1930).

TABLE I

RATES OF FORMATION OF n-C_4H_9MgCl AND C_6H_5MgBr

n-C_4H_9MgCl

Minutes	5	10	20	30	40
Yield, %	20.0	37.9	65.8	78.8	84.0

C_6H_5MgBr

Minutes	1.5	2.25	3.0	3.75	4.50	5.25
Yield, %	33.0	43.9	55.7	63.2	71.8	75.3

The time of reaction for the several alkyl halides was forty-five seconds; the temperature was 40°; and the rate of stirring was 380–390 r. p. m. The results are given in Table II. The rate of formation of t-butylmagnesium bromide (as well as that for benzylmagnesium chloride) could not be determined satisfactorily by the procedure employed because of the significant hydrolysis of the unused halides during analysis to give halogen acids which interfered with the acid titration method of analysis.

TABLE II

RATES OF FORMATION OF SOME ALKYLMAGNESIUM HALIDES

(Time, 0.75 min.)

Halide	n-C_4H_9Cl	n-C_4H_9Br	n-C_4H_9I
Yield, %	5.9	59.1	47.2

Halide	n-C_3H_7Br	n-C_4H_9Br	n-$C_5H_{11}Br$	n-$C_6H_{13}Br$
Yield, %	58.0	59.1	51.1	44.3

Halide	n-C_4H_9Br	i-C_4H_9Br	s-C_4H_9Br
Yield, %	59.1	50.2	46.1

In the rates of formation of some arylmagnesium bromides, the external bath temperature was 45°; the rate of stirring, 1000–1020 r. p. m.; and the time of reaction, six minutes. Internal cooling, at the end of the reaction period, was effected by a cooled mixture of one part of ether and two parts of benzene. The results are given in Table III.

TABLE III

RATES OF FORMATION OF SOME ARYLMAGNESIUM BROMIDES

(Time, 6 min.)

Halide	o-$CH_3C_6H_4Br$	m-$CH_3C_6H_4Br$	p-$CH_3C_6H_4Br$
Yield, %	58.4	60.6	59.0

Halide	α-$C_{10}H_7Br$	β-$C_{10}H_7Br$
Yield, %	30.0	16.7

In addition to the experiments averaged in the three foregoing tables, advantage was taken of the opportunity to confirm earlier work on the yields of the several Grignard reagents under so-called "drop conditions" or "B-conditions," when all of the halide in ether is added to the magnesium in ether after inception of reaction. The results of such control experiments were concordant with those described in THIS JOURNAL, **51**, 1583 (1929).

In the rate studies of organolithium compounds, the general procedure was that used with the Grignard reagent studies mentioned earlier in this paper. Such modifications as are necessary with organolithium compounds are described under the "B-conditions" in the paper on the yields of some organolithium compounds.[3] The quantity of halide used was 0.5 mole; the lithium (0.76 g. or 0.11 atom) was cut in 30–32 pieces; the volume of ether used was 30 cc.; stirring was at the rate of 1400 r. p. m.; the temperature during reaction was 40°; and the time of reaction was one and one-half minutes Reaction was arrested in the usual manner, and internal cooling was effected by the addition of 70 cc. of a cold benzene–ether solution containing 10% of ether.

The average yields, on the basis of "B-conditions" (when the halide is added at once to the lithium in ether after initiating reaction in the customary manner[3]), are given in Table IV.

TABLE IV

RATES OF FORMATION OF SOME ORGANOLITHIUM COMPOUNDS

(Time, 1.5 min.)

Halide	n-C_4H_9Cl	n-C_4H_9Br	C_6H_5Br	C_6H_5I
Yield, %	14.4	68.7	41.2	50.9

Again, advantage was taken of the opportunity to check the earlier "B-conditions."[3] Inasmuch as the present rate studies were run at a slightly higher temperature (40° rather than 25–29°), new values were necessary for "B-conditions" at this more elevated temperature. These are as follows: 76.7% from n-butyl chloride; 49.5% from n-butyl bromide; 94.6% from bromobenzene; and 87.7% from iodobenzene. Comparison with the previous yields at the initially lower temperature shows that the yields under "B-conditions" are increased slightly with the increase in temperature.

These values cannot be compared with those determined by Ziegler and Colonius[2] because of differences in ratios of reactants, temperature and stirring. At 25° and with 100% excess of lithium and 100 cc. of ether for 0.1 mole of halide they obtained the following values with n-butyl chloride: 5% (one hour), 12.8% (two hours), 25% (three hours), 36% (four and one-half hours) and 63.5% (twenty hours). With n-butyl bromide their results were: 7.5% (twenty-five minutes), 17% (one hour) and 19% (two hours or the end of reaction). A correction of a few per cent. was made by them to these values to account for the basic compound formed by the splitting of ether by alkyl-lithium compounds. The basic compound so formed gives, of course, too high values in the acid titration method of analysis, so that the 19% yield with n-butyl bromide is in reality a 15% yield of actual n-butyl-lithium. Their yield of phenyl-lithium from bromobenzene at the end of two hours was 75%. We made no correction for ether splitting because such splitting was undoubtedly quite small in our short time of reaction (one and one-half minutes). Furthermore, such restricted splitting should be relatively of the same order with the n-butyl chloride and n-butyl bromide, the splitting agent being the n-butyl-lithium in each case. Aryl-lithium compounds split ether very slowly, and certainly to an almost negligible extent in one and one-half minutes.

Discussion of Results

When an RX compound reacts with magnesium in ether several reactions can occur. What has been measured is not the relative reactivities of the halides toward magnesium, but the relative

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(3) THIS JOURNAL, **55**, 1252 (1933).

rates of formation of Grignard reagent when RX is added rapidly to magnesium. Under the experimental conditions there is probably relatively little reaction between *pre*-formed RMgX compound and the unused RX compounds employed in this study. When corrections are made for the side reactions or decrease in yield with rapid addition, the same relative order of "rates of formation of Grignard reagent" holds.

Some conclusions which might be drawn from the Grignard reagent studies are the following. (1) The simpler alkylmagnesium bromides form more readily than the simpler arylmagnesium bromides. (2) The rate of formation of *n*-alkylmagnesium bromides decreases with the length of the carbon chain. (3) With a given R group and different halogens, that RX containing chlorine forms the RMgCl compound more slowly than the corresponding RBr compound forms RMgBr. However, the RMgBr appears to form more readily than the RMgI compound. This particular and isolated result may be unexpected, and the problem of secondary reactions might be resolved in a study of the rates of formation of methylmagnesium chloride, bromide and iodide, because there is no significant decrease in yield when methyl iodide is added rapidly to magnesium.[4] (4) The decreasing order of rates of formation of isomeric butylmagnesium bromides is: *n*, *i*, *s*. The slower rate of formation of secondary halides is consistent with the lesser reactivity of halogens in secondary halides.[5] As mentioned in the Experimental Part, the hydrolysis of unused *t*-butyl bromide during analysis prevented inclusion of this compound. (5) There is no essential difference in the rates of formation of *o*-, *m*- and *p*-tolylmagnesium bromides. (6) β-Naphthylmagnesium bromide forms less readily than α-naphthylmagnesium bromide, which in turn forms less readily than the other arylmagnesium bromides investigated.

Mention should be made of the fact that the yields of Grignard reagent at the end of a selected time may or may not be parallel with the times required to *initiate* reaction between an RX compound and magnesium in ether. The times required for starting Grignard formation have been determined with a miscellany of RX compounds.[4] In general, such times are in agreement with the yield values, although there are a few exceptions and notably with the α- and β-bromonaphthalenes.

The following generalizations can be made from the rates of formation of organolithium compounds: (1) the rates of formation follow generally the order of reactivity of the halogen in the RX compound. However, it is known that if the halogen is too reactive as in *n*-butyl iodide no organolithium compound results because of a Wurtz reaction.[2] Methyl iodide is the most striking anomalous case because it gives about 75% yields of methyl-lithium.[3] (2) Alkyl-lithium compounds are apparently formed in higher yields in a given time than aryl-lithium compounds. (3) Where comparisons can be made,[6] organolithium compounds are generally formed more readily than the corresponding Grignard reagent. This does not necessarily mean that when reaction is completed there will be a greater per cent. of organolithium compound. On the contrary, a number of RX compounds give distinctly higher yields of Grignard reagent than of organolithium compound when reaction is completed. For example, the yield of *n*-butyl-lithium from *n*-butyl chloride is 14.4% at the end of one and one-half minutes, whereas a like yield of *n*-butylmagnesium chloride is only obtained at about the end of four minutes, and when each reaction is allowed to run its course under optimal conditions the yield of *n*-butyl-lithium is 77.1% and of *n*-butylmagnesium chloride, 96%. A more direct comparison might be made with aryl-lithium compounds which are known not to cleave the ether used as a solvent. When this is done, it is noted that bromobenzene gives phenyl-lithium in 41.2% yield at the end of one and one-half minutes and phenylmagnesium bromide in 33.0% yield in the same time.

Summary

A study and some generalizations have been made of the rates of formation of some Grignard reagents and organolithium compounds.

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[4] Gilman and Van der Wal, *Bull. soc. chim.*, **45**, 344 (1929). See, also, Rudd and Turner, *J. Chem. Soc.*, 688 (1928), on the comparative reaction of some RX compounds with magnesium.

[5] Conant and Hussey, THIS JOURNAL, **47**, 476 (1925).

[6] It is probable that if the lithium pieces could be cut to form a surface as great as that presented by the magnesium turnings there would be an even greater reactivity of lithium.