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THE EFFECT OF HALIDE IONS IN THE ALKYLATION OF LEAD AND TIN

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SUMMARY

The effect of various nucleophilic species, both neutral and charged, on the alkylation reaction of Pb and Sn by Grignard compounds has been studied. The following activation series has been observed:

$$\text{carbitols} \simeq I^- > \text{tetrahydrofuran, tetrahydrothiophene} > Et_2O \simeq Et_3N \simeq Br^-$$

The activation appears to be associated with the increasing stabilization of the Grignard reagent, and hence with the increasing nucleophilicity of the alkyl group.

INTRODUCTION

In a study of the effect of halide ions on the chemical reactivity of metals, we have examined the alkylation of Pb[1] and Sn[2] with Grignard compounds formed *in situ* by Mg and alkyl halides (RX) in presence of halide ions. The metal–halide interaction has been interpreted as involving the formation of $[ML_nX]$ species, which are known in the case of transition metals[10].

The observed effects can be correlated with those exerted by basic organic compounds, and it is well known that activation by ethers depends upon their basicity[3].

RESULTS AND EXPERIMENTAL

The alkylation presumably proceeds by a two-step mechanism involving the formation of an intermediate Grignard compound:

$$4\,Mg + 4\,RX \rightarrow 4\,RMgX \quad (1)$$

$$M + 4\,RMgX \rightarrow MR_4 + 2\,MgX_2 + 2\,Mg \quad (2)$$

$$M + 2\,Mg + 4\,RX \rightarrow MR_4 + 2\,MgX_2 (M = Sn, Pb) \quad (3)$$

It is known that alkyllead compounds can be prepared from Pb and preformed alkylmagnesium halides[4].

Ethyl bromide was used as both alkylating agent and solvent, in order to avoid secondary effects of a solvent. In spite of its low dielectric constant ($D=9$), it is possible to obtain high salt concentrations in ethyl bromide by using tetrabutylammonium salts[5].

TABLE 1

REACTION CONDITIONS[a] AND RESULTS

Test	Metal M	Catalyst[b]	Molar ratio catalyst/EtBr	Produced MEt_4 (mg)
1	Pb			0
2	Pb	DMC	0.04	684
3	Pb	DEC	0.03	795
4	Pb	DBC	0.02	634
5	Pb	THF	0.06	131
6	Pb	THT	0.01	90
7	Pb	Et_2O	0.5	40
8	Pb	Et_3N	0.04	20
9	Pb	Bu_4NI	0.03	600
10	Pb	Bu_4NBr	0.03	66
11	Pb	Bu_4NClO_4	0.03	0
12	Pb	Bu_4NPF_6	0.07	0
13	Pb	Bu_4NBF_4	0.01	0
14	Pb	Bu_4NBPh_4	0.05	0
15	Sn			0
16	Sn	Et_3N	0.2	80
17	Sn	Bu_4NI	0.02	700
18	Sn	Bu_4NBr	0.07	280

[a] Experimental conditions: T=40°; tests 1–14: Pb 10 g, Mg powder 2.5 g, EtBr 50 ml, time 3 h; tests 15–18: Sn 8 g, Mg powder 2.5 g, EtBr 50 ml, time 7 h. [b] DMC dimethylcarbitol; DEC diethylcarbitol; DBC dibutylcarbitol; THF tetrahydrofuran; THT tetrahydrothiophene.

The results are presented in Table 1. The reaction is very sensitive to the surface state of the metals used. In the case of Pb, the reaction does take place with commercial lead powder, but the best results were obtained by washing this powder with acids (*e.g.*, acetic acid solution in ethanol). It was necessary to prepare tin in spongy form, by displacement with magnesium from solutions of tin (II) chloride in acetone. The alkylation was carried out under N_2 atmosphere with efficient stirring. The quantitative determination of $PbEt_4$ or $SnEt_4$ was carried out by VPC. Two stainless steel columns were used: the first one with a stable phase of 20% silicone oil QF 1 on Chromosorb W and the second with 20% Carbowax 1540 on Chromosorb W and hot wire detector. (T=130°, injector 170°, helium carrier gas, P=1.4 atm, toluene internal standard).

Formation of the Grignard reagent was examined under the same experimental conditions used for the alkylation reactions, and the results are presented in Table 2. The amount of alkylmagnesium halides produced was determined by quantitative VPC analysis of the hydrocarbons evolved on treatment of the reaction mixture with water. These hydrocarbons, which were carried off in a stream of nitrogen, consisted mainly of ethane formed in reaction (4)[6].

$$\mathrm{MgEtBr + H_2O \rightarrow C_2H_6 + MgBrOH} \tag{4}$$

TABLE 2

DECOMPOSITION OF GRIGNARD COMPOUNDS WITH WATER[a]

Test	Catalyst (mmoles)		Composition of the reaction gases (%)			EtBr transf. (mmoles)
			C_2	C_4	H_2	
1			83.9	16.1	traces	16.5
2	Bu_4NI	(10.8)	94.7	2.8	2.5	110.5
3	Bu_4NBr	(12.4)	98.6	1.4	traces	96.5
4	Bu_4NClO_4	(11.7)	90.1	9.9	traces	3.8
5	DEC	(16.5)	96.5	3.5	traces	79.2

[a] Experimental conditions: Mg 4 g; EtBr 50 ml; time 24 h; T 25°.

Small amounts of C_4 hydrocarbons, ethylene and H_2 were also detected. These products arise from the Wurtz reaction (5), and from disproportionation of the Grignard compound[7].

$$EtBr + MgEtBr \rightarrow C_4H_{10} + MgBr_2 \qquad (5)$$

DISCUSSION

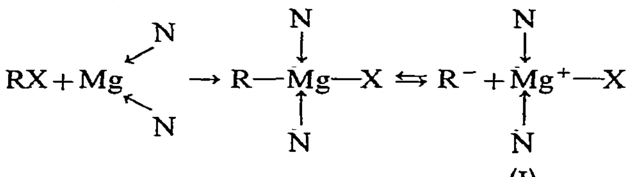
From the data in Table 1 the following activation series can be derived for the alkylation of lead and tin *via* Grignard reagent formation:

$$\text{carbitols} \simeq I^- > \text{THF, THT} > Et_2O \simeq NEt_3 \simeq Br^- \gg ClO_4^-, PF_6^-, BF_4^-, BPh_4^- = 0$$

The activating effect of iodides is therefore comparable with that of basic ethers like carbitols and greater than THF. Bromide ions are comparable with ethyl ether and are less effective than iodides. The absence of alkylation in the presence of ClO_4^-, PF_6^-, BF_4^- or BPh_4^-, enables us to exclude a salt effect. The possibility of a concerted action of tetraalkylammonium cations on the metal to be alkylated (Pb, Sn), as demonstrated by Galli and Olivani[11] for the electrosynthesis of $PbEt_4$, cannot be investigated because of the too low solubility of other halides (*e.g.* LiI or KI) in ethyl bromide.

The compounds used, both charged and neutral, show the same type of activation in alkylmagnesium halide formation (see Table 2) although the differences between the various activators are less marked.

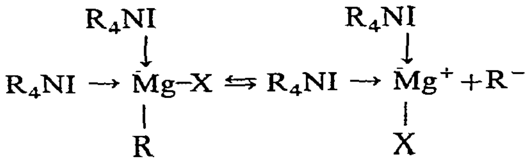
From the results it appears that the nucleophilic agents must be present for the alkylation of lead and tin, which means that the Grignard compound is unable to alkylate the metals in the absence of nucleophilic species. To account for this we suggest that the nucleophiles (N) stabilize the ionic forms (I) and (II) of the Grignard reagent, as in (6):



$$RX + Mg \begin{smallmatrix} \swarrow N \\ \nwarrow N \end{smallmatrix} \rightarrow R{-}\overset{N\downarrow}{\underset{N\uparrow}{Mg}}{-}X \leftrightarrows R^- + \overset{N\downarrow}{\underset{N\uparrow}{Mg^+}}{-}X \qquad (6)$$

(I)

When N is a tetraalkylammonium iodide (R_4NI), the process would be:

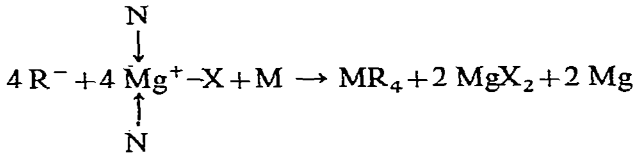


$$R_4NI \rightarrow \underset{\underset{R}{|}}{\overset{\overset{R_4NI}{\downarrow}}{Mg}}{-}X \rightleftarrows R_4NI \rightarrow \underset{\underset{X}{|}}{\overset{\overset{R_4NI}{\downarrow}}{Mg^+}} + R^-$$

(II)

The polarizability of the anions ($I^- > Br^-$) determines the magnitude of the effect.

The carbanion formed in reaction (6) is better able to carry out nucleophilic attack on the metal to be alkylated (7):



$$4\,R^- + 4\,\underset{\underset{N}{\uparrow}}{\overset{\overset{N}{\downarrow}}{Mg^+}}{-}X + M \rightarrow MR_4 + 2\,MgX_2 + 2\,Mg \qquad (7)$$

It is interesting to consider the Nalco process for the formation of $PbEt_4$ and $PbMe_4$[9]. In that process solutions of Grignard compound are electrolysed at Pb electrodes which are kept anodic (*i.e.* electrophilic):

$$Pb(\text{anode}) + 4R^- \rightarrow PbR_4 + 4\,e^- \qquad (8)$$

An analogy can thus be drawn between the electrochemical (8) and the chemical (1) processes in the sense that in the former the alkylation is made easier by keeping the lead anodic, thus increasing electrophilicity of lead, whereas in the latter the alkylation is favoured by increasing the nucleophilicity of the alkyl group of the Grignard reagent.

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