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ORGANOMANGANESE (II) REAGENTS XVII[1]. PREPARATION OF ORGANOMANGANESE BROMIDE COMPOUNDS IN ETHER : AN EFFICIENT AND ECONOMIC ALTERNATIVE TO ORGANOMANGANESE IODIDE COMPOUNDS FOR SYNTHETIC APPLICATIONS

Gérard CAHIEZ * and Blandine LABOUE

Laboratoire de Chimie des Organoéléments, UA 473, tour 44-45
Université P. et M. Curie, 4 Place Jussieu F-75252 PARIS Cédex 05

Abstract : *Organomanganese bromide reagents have been prepared in high yields in ether from organomagnesium or organolithium compounds and manganese bromide. The preparation must be performed in the presence of lithium bromide which allows to dissolve the manganese bromide in ether. Organomanganese bromide reagents react quite similarly to their iodide analogous. For synthetic applications they present the advantage to be clearly cheaper and often more stable.*

These last years, we have shown that, in ether, organomanganese iodide reagents can be acylated, hydroxyalkylated, carbonated... in very high yields[2]. They are especially interesting for their chemoselectivity. However for large scale preparative chemistry, organomanganese iodide reagents present the inconvenient to be prepared from manganese iodide, an expensive material as all iodine derivatives.

On this account, we have envisioned to use manganese bromide instead of manganese iodide. Let us recall that this was not obvious since manganese bromide is not soluble in ether. So, as yet, all our attempts to prepare organomanganese bromide reagents from organomagnesium compounds have led to unsatisfying and unreproducible yields ranging from 30 to 60%[3]. Now we report a way to solve this problem.

To circumvent the previous difficulties, we have tried to solubilize manganese bromide in ether by addition of various complexing agents. Thus, we have discovered that manganese bromide dissolves easily in an ethereal solution of lithium bromide at room temperature. Very likely, an "ate complex" such as $MnBr_3Li$ is formed as in the case of the solubilization of the manganese chloride in THF[4]. It is important to point out that the commercial anhydrous lithium bromide cannot be dissolved in ether, consequently, to have a solution of lithium bromide, it is necessary to prepare it directly in this solvent (e.g. $2\,Li + Br_2 \Rightarrow 2\,LiBr$).

$$\mathbf{MnBr_2 + LiBr}\ \textit{(ethereal solution)}\ \xrightarrow[\textbf{30 min. to 1h}]{\textbf{Ether; 20°C}}\ \mathbf{MnBr_2;\ LiBr}\ \textit{(solution)}$$

As expected, organomagnesium compounds readily react with this manganese bromide-lithium bromide complex[5], in ether, to give the corresponding organomanganese reagents in high yields. Indeed, the reaction mixture is homogeneous and the manganese-magnesium exchange occurs rapidly between 0 and 20°C.

$$\mathbf{MnBr_2;\ LiBr}\ \textit{(solution)}\ \xrightarrow[\textbf{0 to 20°C}]{\textbf{RMgX}}\ \mathbf{RMnBr\ (MgXBr;\ 2\ LiBr)}$$

Instead of preparing a solution of lithium bromide in ether as above, it is more convenient to use commercial lithium bromide (*in solid form*) as follows:

$$\mathrm{RMgX + LiBr} \xrightarrow[\text{20°C, 45 min.}]{\text{Ether}} \underset{(solution)}{\mathrm{RMgX;\ LiBr}} \xrightarrow[\text{20°C; R= alkyl: 45 min., R= aryl or alkynyl: 2 to 3h}]{\mathrm{MnBr_2}} \mathrm{RMnBr} \quad \text{Yields} > 80 \text{ to } 98\%^{6}$$

Effectively, the commercial lithium bromide is insoluble in ether but it dissolves rapidly into an ethereal solution of organomagnesium compound at room temperature. Thereby, the desired organomanganese bromide reagent is formed readily,.in very high yield[6], after addition of manganese bromide, this one being progressively solubilized in the reaction mixture owing to the presence of lithium bromide.

From the previous results, it was easy to understand that organomanganese reagents are readily prepared from manganese bromide and organolithium compounds prepared in ether. Indeed, these one are associated to one equivalent of lithium halide ($RX + 2\,Li \Rightarrow RLi + LiX$; $X = Br, I$) which allows to dissolve the manganese bromide.

$$\mathrm{RLi;\ LiBr + MnBr_2} \xrightarrow[\text{10°C, 30 min.}]{\text{Ether}} \underset{(solution)}{\mathrm{RMnBr;\ 2\ LiBr}} \quad \text{Yields} > 74 \text{ to } 96\%^{6} \ \text{(R= Alkyl, alkenyl, alkynyl, aryl...)}$$

Interestingly, commercial solutions of organolithium compounds in hydrocarbons (*i.e. BuLi / Hexane*) can also be used though they do not contain lithium halide. In this case, the reaction probably begins on the surface of the manganese bromide then, this one is progressively dissolved, by virtue of the formation of lithium bromide in the reaction mixture, and the metal-metal exchange reaction rate gradually accelerates.

$$\mathrm{BuLi\ /\ Hexane + MnBr_2} \xrightarrow[\text{10°C, 30 min.}]{\text{Ether}} \left[BuLi + MnBr_2 + BuMnBr + LiBr \right] \longrightarrow \underset{> 95\%^{6}}{\mathrm{BuMnBr;\ LiBr}}$$

In conclusion, a large variety of alkyl, alkenyl, alkynyl and aryl manganese bromide reagents can be now easily prepared in ether from organomagnesium (*and organolithium*) compounds in nearly quantitative yields. For synthetic purposes, this is a clear improvement. As a matter of fact, they will be profitably used in place of their iodide counterparts since they react similarly[7] and they offer the following advantages :

- organomanganese bromide reagents are obtained from manganese bromide which is clearly less expensive and more available than manganese iodide
- the absence of iodide in the reaction mixture allows to avoid the liberation of iodine sometimes observed during the final work up. This is especially important in the case of iodine-sensitive products, for instance:

$$\mathrm{BuC{\equiv}CMnX + MeCH{=}CHCOCl} \xrightarrow[\text{20°C, 2h}]{\text{Ether}} \mathrm{BuC{\equiv}CCOCH{=}CHMe}$$

$$\text{From } \mathrm{MnI_2} : 0\% \qquad \text{From } \mathrm{MnBr_2} : 87\%$$

Finally, it should be emphasized that the presence of both lithium and magnesium salts has a stabilizing effect on the organomanganese bromide reagents[8].

References and Notes

1. G. Cahiez, B. Laboue and P. Tozzolino, French Patent Application n° 8816598; 1988 (Elf Aquitaine) For part XVI see G. Cahiez and M. Alami, Tetrahedron Lett., preceding letter.
2. G. Cahiez and J. Normant in "*Modern Synthetic Methods 1983*", Ed. R. Scheffold, J. Wiley and Sons, Inc. Chichester,1983, 3,173.
3. This is due to a too long and uncertain reaction time. Thus, organomanganese bromide reagents decompose partially or the reaction is not complete.
4. The preparation of the "ate" complex $MnCl_4Li_2$ is described in: G. Cahiez and M. Alami, Tetrahedron, in press.
5. To prepare organomanganese bromides from organomagnesium compounds in ether it is also possible to use a complex manganese bromide-tetraalkylammonium bromide (*i.e.* $Bu_4NBr;MnBr_2$) which is partially soluble.
6. Based on the yields of ketones obtained after acylation of various RMnBr by BuCOCl.
7. All the reactions previously described with RMnI can be performed with the corresponding RMnBr. The yields are similar or even higher.
8. For example, in the presence of lithium or magnesium salts alone, in ether, the decomposition of butylmanganese halides begins after 30 min. at 20°C whereas, in the presence of both lithium and magnesium salts, no decomposition occurs after 2h at 20°C.

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