Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ON THE ACTION OF HALOGENS UPON GRIGNARD AND IOTSICH REAGENTS

L. I. ZAKHARKIN, V. V. GAVRILENKO AND B. A. PALEY
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (USSR)

(Received September 20th, 1969)

SUMMARY

Chlorination of Grignard and Iotsich reagents, RMgX, (where X = Br, I) gives considerable quantities of RI and RBr together with RCl. Bromination of RMgI results in RI and RBr. Bromination of RMgCl leads to RBr, and iodination of RMgX (X = Cl, Br), to RI.

A method is proposed for the preparation of RC≡CCl by the reaction of chlorine with RC≡CMgCl.

It is now accepted[1,2] that in general the action of halogens on Grignard reagents involves the substitution of magnesium halide with halogen:

$$\text{RMgX} + \text{X}'_2 \rightarrow \text{RX}' + \text{XMgX}'$$
$$(\text{X}, \text{X}' = \text{Cl, Br, I})$$

The reaction of halogens with Iotsich reagents is assumed to proceed analogously[1,3].

$$\text{RC}{\equiv}\text{CMgX} + \text{X}'_2 \rightarrow \text{RC}{\equiv}\text{CX}' + \text{XMgX}'$$

We have found that these assumptions require clarification. The reaction of chlorine with Grignard and Iotsich reagents follows the above schemes only when magnesium is combined with chlorine:

$$\text{RMgCl} + \text{Cl}_2 \rightarrow \text{RCl} + \text{MgCl}_2$$
$$\text{RC}{\equiv}\text{CMgCl} + \text{Cl}_2 \rightarrow \text{RC}{\equiv}\text{CCl} + \text{MgCl}_2$$

When bromine and iodine are combined with magnesium, the reaction with chlorine proceeds in accordance with the schemes:

$$\text{RMgX} + \text{Cl}_2 \rightarrow \text{RX} + \text{RCl} + \text{MgXCl} + \text{MgCl}_2$$
$$(\text{X} = \text{Br, I})$$
$$\text{RC}{\equiv}\text{CMgX} + \text{Cl}_2 \rightarrow \text{RC}{\equiv}\text{CX} + \text{RC}{\equiv}\text{CCl} + \text{MgXCl} + \text{MgCl}_2$$

Examples investigated in the present work are shown in Table 1. The results obtained testify that chlorine reacts with RMgBr and RMgI to produce predominantly RBr and RI, respectively, and RCl only in smaller quantities. The application of

TABLE 1

CHLORINATION AND BROMINATION OF GRIGNARD AND IOTSICH REAGENTS

RMgX	Halogen	Composition of halogenation products (%)	
C_6H_5MgBr	Cl_2	C_6H_5Cl–48	C_6H_5Br–52
C_6H_5MgI	Cl_2	C_6H_5Cl–26	C_6H_5I–74
n-$C_6H_{13}MgBr$	Cl_2	n-$C_6H_{13}Cl$–40	n-$C_6H_{13}Br$–60
n-$C_7H_{15}MgI$	Cl_2	n-$C_7H_{15}Cl$–25	n-$C_7H_{15}I$–75
α-$C_{10}H_7MgI$	Cl_2	α-$C_{10}H_7Cl$–48	α-$C_{10}H_7I$–52
$C_6H_5C\equiv CMgBr$	Cl_2	$C_6H_5C\equiv CCl$–22	$C_6H_5C\equiv CBr$–78
$C_6H_5C\equiv CMgI$	Cl_2	$C_6H_5C\equiv CCl$–30	$C_6H_5C\equiv CI$–70
n-$C_4H_9C\equiv CMgBr$	Cl_2	n-$C_4H_9C\equiv CCl$–38	n-$C_4H_9C\equiv CBr$–62
n-$C_4H_9C\equiv CMgI$	Cl_2	n-$C_4H_9C\equiv CCl$–49	n-$C_4H_9C\equiv CI$–51
C_6H_5MgI	Br_2	C_6H_5Br–21	C_6H_5I–79
n-$C_7H_{15}MgI$	Br_2	n-$C_7H_{15}Br$–42	n-$C_7H_{15}I$–58
$C_6H_5C\equiv CMgI$	Br_2	$C_6H_5C\equiv CBr$–53	$C_6H_5C\equiv CI$–47

the reaction of chlorine with a Grignard reagent for the preparation of RCl from RBr or RI therefore appears to be unreasonable.

In spite of a report that $RC\equiv CCl$ can not be prepared by the reaction of chlorine with an Iotsich reagent[3] we have found that chlorination of $RC\equiv CMgCl$ gives more than 80% of acetylene chlorides. Thus, phenylacetylene gives 85% of phenylacetylene chloride, and butylacetylene gives 80% of butylacetylene chloride.

$$C_6H_5C\equiv CMgCl + Cl_2 \xrightarrow[-60^\circ]{} C_6H_5C\equiv CCl + MgCl_2$$

Thus, not only iodo- and bromo-, but also chloroacetylenes can be conveniently obtained via Iotsich reagents.

It has been reported that the reaction of C_6H_5MgBr and chlorine leads to an exceptionally explosive product[4]. We have found that in ethereal and tetrahydrofuran solutions this reaction proceeds without the formation of any explosive product.

The reactions of Grignard and Iotsich reagents with bromine occur in the "regular" manner when magnesium is combined with chlorine or bromine:

$$RMgX + Br_2 \rightarrow RBr + MgBrX$$

$$(X = Cl, Br)$$

$$RC\equiv CMgX + Br_2 \rightarrow RC\equiv CBr + MgXBr$$

When iodine is bonded with magnesium the reaction with bromine gives, predominantly, iodide, with a smaller quantity of bromide (Table 1).

$$RMgI + Br_2 \rightarrow RI + RBr + MgIBr + MgBr_2$$

$$RC\equiv CMgI + Br_2 \rightarrow RC\equiv CI + RC\equiv CBr + MgIBr + MgBr_2$$

These results show that in the reaction of the Grignard reagent with bromine one can transfer from RCl to RBr although there is no reason to employ this reaction for the preparation of RBr from RI.

Iodine always reacts with the Grignard and Iotsich reagents in the "regular" manner substituting the MgX fragment with iodine:

$$RMgX + I_2 \rightarrow RI + MgXI$$

$$(X = Cl, Br, I)$$

$$RC{\equiv}CMgX + I_2 \rightarrow RC{\equiv}CI + MgXI$$

The reactions of halogens with Grignard and Iotsich reagents were studied in diethyl ether and tetrahydrofuran.

The formation of RBr and RI in the reaction of chlorine with RMgX where $X = Br$, I, and the formation of RI in the reaction of bromine with RMgI might be explained, along with C–Mg bond cleavage by halogen, by considerable halogen exchange in the MgX fragment of RMgX or MgX_2 resulting in ClBr, ClI, BrI or Br_2 and I_2. The latter in turn may further react with the C–Mg bond. Evidence in support of this suggestion may be found in the formation of bromine and iodine when chlorine is bubbled through a solution of $MgBr_2$ or MgI_2 in tetrahydrofuran.

EXPERIMENTAL

The Grignard and Iotsich reagents were obtained by the usual procedure and their concentrations determined by an acid titration. Solutions of Grignard reagents were analysed after hydrolysis in order to show the absence of the initial alkyl or aryl halides.

Chlorination of RMgX

Chlorine (0.01 *M*) was passed from a weighted trap into a solution of RMgX (0.01 *M*) in ether or tetrahydrofuran with vigorous stirring at −60°. The mixture was then heated to 10–15°, decomposed with dilute HCl and extracted with ether. The composition of the product was analyzed by GLC.

After the chlorination of Iotsich reagents, the reaction mixture was decomposed at −60° with dilute HCl and treated rapidly with sodium thiosulfate solution to remove free bromine or iodine.

Phenylchloroacetylene

6.4 g (0.09 *M*) of chlorine was passed into a solution of 0.09 *M* of $C_6H_5C{\equiv}CMgCl$ (prepared from phenylacetylene and C_2H_5MgCl) free from bromide and iodide in tetrahydrofuran with stirring at −60°. The mixture was decomposed with dilute HCl and mixed with ether. The organic layer was washed with $NaHCO_3$ solution and water. After distillation *in vacuo*, 10.4 g (85%) of phenylchloroacetylene was obtained, b.p. 72–74° at 15 mm.

n-Butylchloroacetylene

This was prepared similarly to phenylchloroacetylene from 0.1 *M* of $n\text{-}C_4H_9\text{-}C{\equiv}CMgCl$ (obtained from butylacetylene and C_2H_5MgCl), free from bromides and iodides; 9.3 g (80%) of n-butylchloroacetylene was obtained, b.p. 44–46° at 50 mm.

Bromination of RMgX

A solution of 0.01 *M* of bromine was added dropwise with stirring at −50° to RMgX (0.01 *M* in ether or tetrahydrofuran). The mixture was then heated to room temperature, decomposed with dilute HCl, extracted with ether and analyzed by GLC.

Iodination of RMgX

An etheral solution of 0.01 *M* of iodine was added dropwise with stirring to a solution of 0.01 *M* of RMgX at 0°. The mixture was decomposed with dilute HCl at room temperature. The treatment and analysis of the reaction products were similar to those in the bromination of RMgX.

REFERENCES

1 M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York, 1954, p. 1332.
2 S. T. Ioffe and A. N. Nesmeyanov, *Metody elementoorganicheskoi khimii*, Moscow, 1963, p. 81.
3 L. D. Bergel'son, *Reactsii i metody issledovaniya organicheskikh soedinenii*, Vol. 4, Moscow, 1956, p. 25.
4 R. L. Datta and H. K. Mitter, *J. Amer Chem. Soc.*, 41 (1919) 287.