

# FUNDAMENTALS OF ORGANIC CHEMISTRY

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*A.N. NESMEYANOV, N.A. NESMEYANOV*

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*Volume IV*

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А. Н. Несмеянов, Н. А. Несмеянов

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ОРГАНИЧЕСКОЙ  
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## **PART TWO**



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# Organoelement Compounds

The first organometallic compounds had been discovered by the middle of last century. They were investigated in a systematic way by Frankland. These volatile compounds, whose vapour density could be measured and molecular weights determined, were used by Frankland for establishing the concept of valency. A metal in such compounds is linked by a chemical bond to a carbon atom of an organic (aliphatic or aromatic) radical.

There is no sharp boundary line between metals and nonmetals (metalloids). This boundary line is even less pronounced in their organic derivatives, so that the simplest carbon-containing derivatives of the following elements show points of similarity: Bi, Sb, As, and P; Sn, Ge, and Si; Al and B, which can be seen even from the similarity between the forms of compounds of elements of varying degree of alkylation (or arylation). Examples are given in Table 12.1.

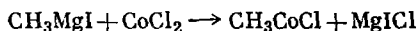
TABLE 12.1

Group IV	Group V
RSiH <sub>3</sub> , R <sub>2</sub> SiH <sub>2</sub> , R <sub>3</sub> SiH, R <sub>4</sub> Si RSiCl <sub>3</sub> , R <sub>2</sub> SiCl <sub>2</sub> , R <sub>3</sub> SiCl	RPH <sub>2</sub> , R <sub>2</sub> PH, R <sub>3</sub> P RPH <sub>2</sub> , R <sub>2</sub> PH RPH <sub>2</sub> , R <sub>2</sub> PH, R <sub>3</sub> P
RGeH <sub>3</sub> , R <sub>2</sub> GeH <sub>2</sub> , R <sub>3</sub> GeH, R <sub>4</sub> Ge RGeCl <sub>3</sub> , R <sub>2</sub> GeCl <sub>2</sub> , R <sub>3</sub> GeCl	RAsH <sub>2</sub> , R <sub>2</sub> AsH, R <sub>3</sub> As RAsCl <sub>2</sub> , R <sub>2</sub> AsCl RAsCl <sub>2</sub> , R <sub>2</sub> AsCl <sub>3</sub> , R <sub>3</sub> AsCl <sub>2</sub> , R <sub>4</sub> AsCl, R <sub>5</sub> As
RSnH <sub>3</sub> , R <sub>2</sub> SnH <sub>2</sub> , R <sub>3</sub> SnH, R <sub>4</sub> Sn RSnCl <sub>3</sub> , R <sub>2</sub> SnCl <sub>2</sub> , R <sub>3</sub> SnCl	RSbH <sub>2</sub> , R <sub>2</sub> SbH, R <sub>3</sub> Sb RSbCl <sub>2</sub> , R <sub>2</sub> SbCl RSbCl <sub>2</sub> , R <sub>2</sub> SbCl <sub>3</sub> , R <sub>3</sub> SbCl <sub>2</sub> , R <sub>4</sub> SbCl, R <sub>5</sub> Sb
RPbH <sub>3</sub> , R <sub>2</sub> PbH <sub>2</sub> , R <sub>3</sub> PbH, R <sub>4</sub> Pb RPbCl <sub>3</sub> , R <sub>2</sub> PbCl <sub>2</sub> , R <sub>3</sub> PbCl	

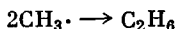
The area of organometallic compounds was increasingly expanding, being transformed about the middle of this century into **organoelement**, or **elementoorganic chemistry**, i.e., the chemistry of organic compounds of all the elements. The field of organoelement compounds is basically the field of carbon compounds of the elements, which are unusual for classical organic chemistry, the latter being defined as the chemistry of the elements called organogens (carbon, hydrogen, oxygen, nitrogen, sulphur, chlorine, bromine, iodine, and phosphorus in the form of phosphoric acid esters). Phosphorus thus stands, as it were, at the boundary line between the two areas of organic chemistry. Naturally, each element is present in an organic molecule in the form of one or more functional groups. This will supplement our knowledge of the functional groups—derivatives of the organogenetic elements.

The great majority of the elements of the periodic system are metals. Therefore, more than half of the compounds of organoelement chemistry are **organometallic compounds**. Organometallic compounds are defined as substances in which the carbon atom is directly linked (through a covalent or ionic bond) to the metal involved. But not all metals form stable alkyl compounds. It is mainly non-transition metals that form such compounds (with the exception of Au and Pt).

If an attempt is made to synthesize an alkyl compound of a transition metal, say, cobalt, by means of an exchange reaction:



then the resulting alkyl derivative of cobalt will decompose even at a temperature below  $0^\circ\text{C}$ :

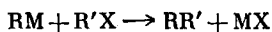


With a few exceptions, there exist no stable, purely alkyl or purely aryl compounds of transition metals. Transition metals, however, are known to form other types of compounds with a direct carbon-metal bond. These substances are structurally related to inorganic complex compounds. Among them are, for example, the long-known complex cyanides,  $\text{K}_4\text{Fe}(\text{CN})_6$ . They also include metal carbonyls, such as  $\text{Fe}(\text{CO})_5$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{Cr}(\text{CO})_6$ , etc. Closely related to them are the so-called  $\pi$ -complexes of olefins with transition metals. All these compounds will be discussed at a later time.

## 12.1. Active Organometallic Compounds of Groups I, II, and III

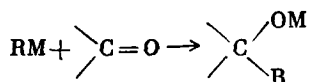
The alkyl and aryl compounds of alkali and alkaline-earth metals, Be, Mg, Zn, Cd, and Al are decomposed by acids, water, and alcohols with the evolution of a hydrocarbon, are oxidized by molecular oxygen, react with carbonyl compounds and enter into a large variety of reactions with other oxygen, sulphur, and nitrogen functional groups, in which the carbon-metal bond is broken. In all these reactions they differ from the alkyl and aryl compounds of Hg, In, Tl, Si, Ge, Sn, Pb, As, Sb, Bi. Organometallic compounds of the alkali metals (except organolithium compounds) are ionic compounds and their reactivity is due to the alkyl (or aryl) anion. Although other active organometallic compounds have a covalent carbon-metal bond, it is so strongly polarized ( $\overset{\delta-}{\text{C}}-\overset{\delta+}{\text{M}}$ ) that their reactions are generally similar to those of ionic compounds, though they proceed not so vigorously as the latter.

Thus, organic compounds of the alkali metals (except RLi) react with alkyl halides and with aryl halides:



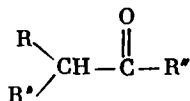
Even organomagnesium compounds react in this way only with allyl halides, benzyls and other types of compounds having a mobile halogen atom (the  $\alpha$ -halogen atom of halosubstituted acids, esters, etc.).

Active organometallic compounds react with carbon dioxide by the well-known reaction, forming acids, but organoaluminium and organozinc compounds give this reaction only under more severe conditions. The normal reaction of active organometallic compounds with carbonyl compounds proceed according to the following scheme:

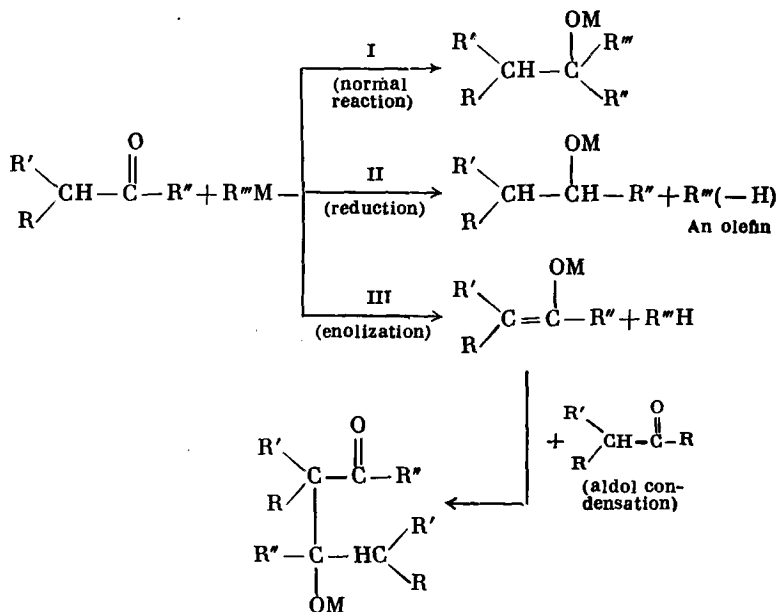


This reaction, however, is accompanied by certain complications (which will be considered in more detail when dealing with organomagnesium compounds), which are especially characteristic of the most active compounds of this kind, i.e., ionic active organometallic compounds or those more closely related to them.

In the case of carbonyl compounds of the general structure

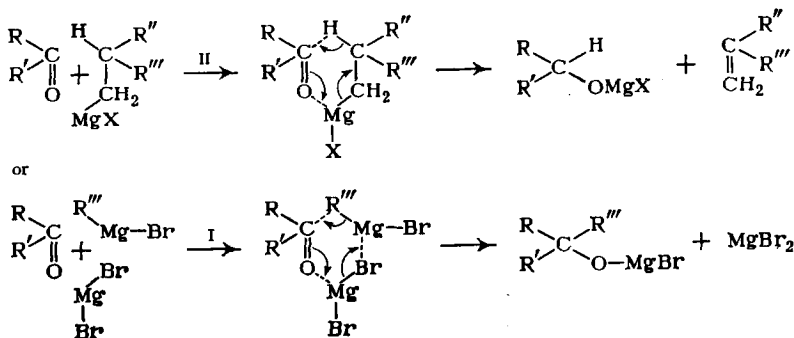


the reaction may proceed in several directions, and whether this or that direction predominates depends on the nature of the radical (its electronegativity), the metal, the radical-metal bond (the degree of ionic character), and on the steric hindrances created by the radicals  $R$ ,  $R'$ ,  $R''$ , and  $R'''$ :



The steric hindrances suppress the normal reaction I and have little effect on reactions II and III. For reaction II (reduction by hydrogen due to  $R'''$ ) to be accomplished it is necessary that the radical  $R'''$  contain a  $\beta$ -hydrogen capable of migrating in the form of a hydride ion to the carbonyl compound so that the radical  $R''$  could be converted into olefin  $R''$  (minus H). For reaction III to take place, the carbonyl compound must contain a hydrogen atom. Organosodium and organopotassium compounds predominantly react by path III if only the carbonyl compound involved has an  $\alpha$ -hydrogen atom. The route taken by the reactions of organolithium and organomagnesium compounds depends on the nature of the radical attached to the metal. The least complicated are the reactions of methyl, benzyl, phenyl, and acetyl derivatives, which take route I; the most complicated are the reactions of compounds with aliphatic and alicyclic secondary radicals, which take route II and, depending on the type of carbonyl compound, by route III. The side reactions (II) as well as the main reaction (I) probably proceed via the six-membered reaction complex (transition state) which may involve an

additional molecule of  $\text{MgX}_2$ :



## 12.2. Group I of the Periodic System

**Organometallic Compounds of the Alkali Metals.** 1. Alkyl and aryl halides react with the alkali metals in inert solvents (hexane, octane, and also benzene for lithium), forming alkyl and aryl derivatives of alkali metals. The situation, however, is complicated even in the case of sodium by the Wurtz reaction which proceeds through stage (1) and further by reaction (2); for potassium the reaction can seldom be stopped at stage (1):



The compounds  $\text{RNa}$  thus obtained can be used for many (but not for all) types of reactions similar to reactions of Grignard reagents (P. P. Shorygin, Morton). Since organolithium compounds are more convenient to handle and are also more soluble than all the organic compounds of the other alkali metals, they find wide application in synthetic work, especially in syntheses involving Grignard reagents. Besides, the synthesis of organolithium compounds presents less difficulties in choosing the solvent: they can be prepared both in paraffin hydrocarbons and in benzene, and in many cases (methyl-lithium, phenyllithium) even more preferably in ether.

Alkylsodium and arylsodium compounds and the corresponding compounds of potassium are solid colourless ionic substances which are insoluble in solvents. Benzylsodium and triphenylmethylsodium are soluble in ether, have a cherry-red colour (the colour of the anion), and their solutions are conductors of electricity. Methyl-lithium, ethyllithium, and aryllithium are solid compounds, but other lithium alkyls are liquids. They are all soluble in inert solvents. Benzyl-lithium and triphenylmethyl-lithium are similar to the corresponding



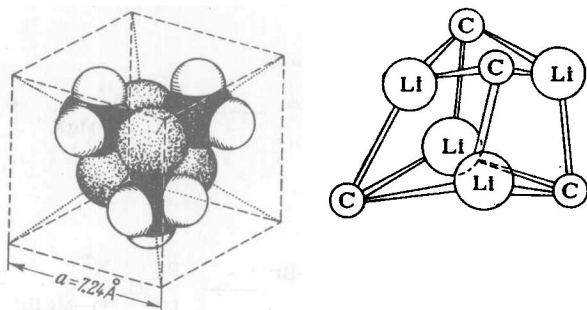


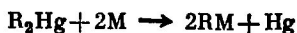
Fig. 12.1.

The models of the methyl-lithium tetramer (hydrogen atoms not shown).

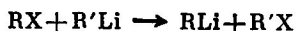
compounds of sodium. The compounds of potassium, rubidium and cesium have been studied much less thoroughly. Lithium alkyls are in the associated state in solutions (the degree of their polymerization varies from 2 to 6), and methyllithium is a tetramer (Fig. 12.1) in which not electron pairs but multicentre orbitals are involved in the formation of bonds. The carbon atoms in  $(\text{CH}_3\text{Li})_4$  have a coordination number of 5. Bridging methyl groups of this kind will be dealt with in discussing organoaluminium compounds, and bridging hydrogens—in the treatment of boron hydrides. All alkyl and aryl compounds of the alkali metals are spontaneously inflammable in air, are decomposed vigorously under the influence of alcohols, water and acids.

Apart from the above-described synthesis from halogen derivatives and a metal, the simplest organic compounds of the alkali metals can be obtained by the following methods.

2. The action of a metal on organomercury compounds:



3. The reaction of lithium alkyls with aryl or alkyl halides:



4. The direct **metalation** (i.e., the replacement of hydrogen by a metal) involving the action of alkyl derivatives of the alkali metals on aromatic hydrocarbons (the Shorygin reaction which has been thoroughly worked out for lithium by Gilman) and, in general, on substances with a mobile hydrogen atom. For example,

