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Reaction of sodium diethylphosphite with Group VIB hexacarbonyls

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The interaction of sodium diethylphosphite with the hexacarbonyl complexes of chromium-group metals occurs as a nucleophilic attack of the diethylphosphite anion at the carbon atom of the carbonyl groups as well as to the generation of the phosphaorganometallic species that are catalytically active in the phosphorylation of tetrachloroethylene.

The substantial positive charge of the carbon atom in the hexacarbonyls of chromium-group metals(0) opens the possibility of a nucleophilic attack towards their carbonyl groups.[1] This process leads to the formation of various organometallic anions (either stable or metastable) that are able to act as the intermediates of different catalytic procedures.[2] The reactions of the metal hexacarbonyls with O-,[3] C-[4] and N-nucleophiles[5] were described but the reactivity of these complexes in the processes with P-nucleophiles remains unknown.

Earlier, we reported on the interaction of dialkylphosphites with metal(0) hexacarbonyls either in polar and in non-polar media.[6] Here we present the results of a study of the interaction of the diethylphosphite anion with the homoligand carbonyl complexes of Group VIB metals.

The above interaction was held in an ethanol solution of metal(0) hexacarbonyls having a two- or threefold excess of diethylphosphoric acid towards the carbonyl complex used. The diethylphosphite anion was introduced in the reaction mixture as sodium diethylphosphite. After the mixing of all the reactants, the reaction mixture obtained was refluxed in a flow of dry argon. The reaction mixtures were studied by dynamic ^{31}P NMR and IR spectroscopy. In the ^{31}P NMR spectra of the reaction mixtures, the singlet signal appears and grows downfield relative to the dialkylphosphites signals. The chemical shifts of the signals are 112, 148 and 152 ppm for the mixtures derived from the complexes $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, respectively. Such chemical shifts match the trivalent three-coordinated phosphorus chemical shifts. We did not observe the splitting of the phosphorus signals that can be caused by the interaction of the nucleus ^{31}P with the magneto-active nuclei ^{95}Mo and ^{183}W. This observation allows us to exclude the possibility of phosphorus coordination with the transition metals. According to ^{31}P NMR spectroscopy data, the reflux of the reaction mixture over 8 h results in the complete consumption of sodium diethylphosphite in the reaction with molybdenum(0) hexacarbonyl, while in the reaction mixtures containing the organometallic derivatives of chromium or tungsten some residual signals of sodium diethylphosphite were observed. This observation is

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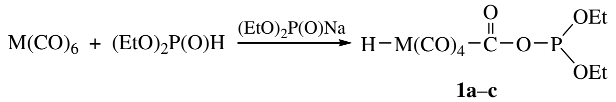
in agreement with the reported earlier greater reactivity of the [illegible] lex either in the ligand exchange or in nucleo[illegible] ctions.[7]

[illegible] tra of the reaction mixtu[illegible] hexacarbonyl show the appearance and growth [illegible] of the sharp band at 1700 cm^{-1} matching the oscillation of the C=O fragment in the ester group. Collaterally to this signal the weak band at 2368 cm^{-1} appears and grows in the IR spectra of the reaction mixture. According to published data,[8] we referred this band to the vibrations of the Mo–H bond. The study of the same reaction mixture by chromatography–mass spectroscopy allowed us to fix the organometallic component in the reaction mixture whose molecular ion has *m/z* 376 ($C_9H_{11}O_8PMo$).

The results of the spectral investigations of the products of the diethylphosphite-anion interaction with the hexacarbonyls allow us to propose the addition of the dialkylphosphite anion towards the electrophilic carbon atom of the carbon monoxide ligands. This addition leads to the formation of metal hydrides **1a–c**. The abmident phosphite anion acts as an O-nucleophile.



$$M(CO)_6 + (EtO)_2P(O)H \xrightarrow{(EtO)_2P(O)Na} H{-}M(CO)_4{-}C(=O){-}O{-}P(OEt)_2$$

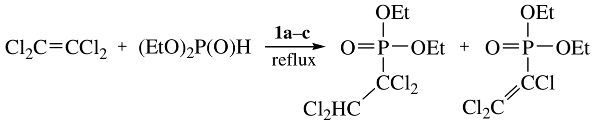
1a–c

a M = Cr
b M = Mo
c M = W

The synthetic results are the first example of the interaction of phosphorus-containing nucleophilic species with the carbonyl complexes of chromium-group metals resulting in the nucleophilic attack towards the positively charged carbon atoms of the carbonyl ligand rather than the substitution of the carbon monoxide.

Compounds **1a–c** show catalytic activity in the interaction of tetrachloroethylene and diethylphosphite.

The injection of compouds **1** to the mixture containing equimolar quantities of tetrachloroethylene and diethylphosphite with the following heating at 120 °C in a sealed ampoule in dry argon for 6 h leads to the total conversion of diethylphosphite.

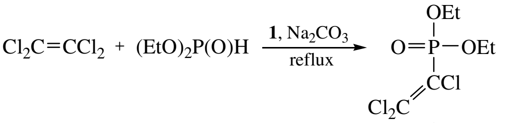


$$Cl_2C{=}CCl_2 + (EtO)_2P(O)H \xrightarrow[\text{reflux}]{\textbf{1a–c}} Cl_2HC{-}CCl_2{-}P(O)(OEt)_2 + Cl_2C{=}CCl{-}P(O)(OEt)_2$$

2 **3**

After the conversion of the dialkylphosphite, we monitored in the remaining reaction mixture only two organophosphorus products of the interaction of tetrachloroethylene with diethylphosphite catalysed with phosphaorganometallic species **1**. They are 1,1,2,2-tetrachloroethyl-*O*,*O*-diethylphosphonate **2** [δ_P 9.3 (s), *m/z* 302 [M]$^+$ (78%), 304 (100%), 306 (49%)] and 1,2,2-trichlorvinyl-*O*,*O*-diethylphosphonate **3** [δ_P 5.7 (s), *m/z* 266 [M]$^+$ (100%), 268 (96%), 270 (31%)]. The ratio of the product of the addition of diethylphosphite to the double bond of tetrachloroethylene **2** and tetrachloroethylene dechlorophosphorylation product **3** is equal to 2:1 when the process is held in the sealed ampoule in the absence of the basic additives.

The interaction of diethylphosphite and tetrachloroethylene in the presence of complexes **1** and sodium carbonate leads to the formation of a single organophosphorus compound – the product of tetrachloroethylene dechlorophosphorylation – vinylphosphonate **3**.



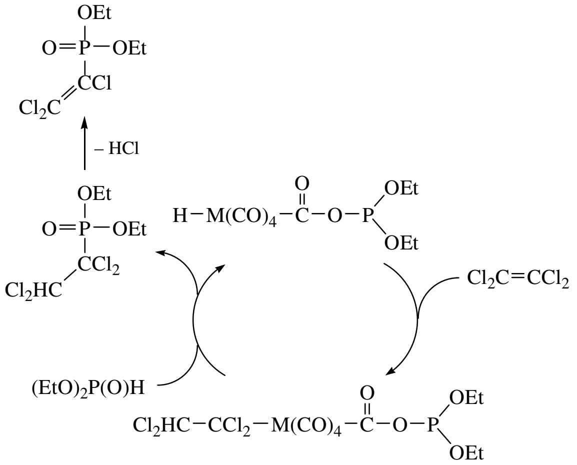
$$Cl_2C{=}CCl_2 + (EtO)_2P(O)H \xrightarrow[\text{reflux}]{\textbf{1}, Na_2CO_3} Cl_2C{=}CCl{-}P(O)(OEt)_2$$

3

The treatment of a mixture containing both 1,1,2,2-tetrachloroethyl-*O*,*O*-diethylphosphonate **2** and 1,2,2-trichloroethenyl-*O*,*O*-[illegible] **3** with sodium carbonate also produces the [illegible] us compound **3**. This substance is the most attractive [illegible] dialkylvinyl phosphonates are important monomers for copolymerization.[9]

One can suppose that the formation of substitution product **3** in the cases described above occurs according to the addition–elimination mechanism. The reaction in the sealed vessel and in the absence of bases prevents the hydrogen chloride elimination and allows us to observe the product **2** of diethylphosphite addition towards the C=C bond.

The catalytic role of phosphaorganometallic species **1** in the process of the addition product formation is apparently due to the electrophilic addition of the M–H bond to the double tetracholethylene bond. The dehydrochlorination of the adduct, proceeding with the degree depending on the reaction conditions leads to the corresponding product of vinyl chlorine substitution with the P-nucleophile.



Note that the heterolytic phosphorylation of the perhaloalkenes cannot be employed to the non-coordinated unsaturated polyhalogeno-containing compounds. This is the only example of the radical addition of hydrophosphoryl compounds to tetrafluoroethylene.[10] The addition mentioned is promoted with the peroxide catalysts and is accompanied with the auxiliary processes. On the contrary, the method of the haloalkyl- and halovinylphosphonates synthesis described has the high efficiency.

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