Addition of Dialkyl Hydrogen Phosphites to Alkenes in the Presence of Carbonyl Complexes of Chromium Subgroup Metals and Iron

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Received September 28, 2000

Abstract — Depending on the reactant ratio and order of their mixing, reactions of dialkyl hydrogen phosphite with alkenes in the presence of catalytic amounts of homoligand carbonyl complexes of iron or chromium subgroup metals yield phosphonates by two pathways: reaction of dialkyl hydrogen phosphite with π -coordinated alkene and addition to alkene of the product of reaction of dialkyl hydrogen phosphite with the transition metal carbonyl. The products of reactions of Fe(CO)₅ and W(CO)₆ with dialkyl hydrogen phosphites contain the phosphorus–metal bond.

Addition of hydrophosphoryl compounds across double bonds (Pudovik reaction) occurs only under conditions of homolytic or electrochemical activation if the unsaturated molecule contains no strong electron-withdrawing substituents [1, 2]; this fact noticeably limits the synthetic potential of this very convenient route of phosphorylation of organic substrates. Therefore, it is urgent to develop catalytic systems for addition of P-nucleophiles to carbon-carbon multiple bonds inert to nucleophilic attack. Recent papers [3, 4] reported on catalytic addition of phosphines and phosphites to nonactivated alkenes in the presence of homoligand phosphine complexes of zerovalent platinum metals. It is known that coordinated alkenes in transition metal π complexes containing also electronacceptor ligands (e.g., carbonyls) become electrondeficient and hence more susceptible to a nucleophilic attack [5]. However, there are no published data about formation of alkylphosphonates by reaction of dialkyl hydrogen phosphites with transition metal π complexes.

To examine the possibility of hydrophosphorylation of nonactivated alkenes in the coordination sphere of transition metals, we prepared π complexes of cyclohexene with Fe(CO)₅, W(CO)₆, Mo(CO)₆, and Cr(CO)₆. To prepare η^2 -(alkene)pentacarbonylchromium(0), -molybdenum(0), and -tungsten(0), we used both thermal and photochemical activation, and with Fe(CO)₅ only the photochemical procedure was used, because on heating iron π complexes with carbonyl ligands and Fe(CO)₅ tend to transform into polynuclear complexes and even degrade [6].

The reaction products were characterized by ¹H

NMR and IR spectroscopy. The upfield shift of the signals of hydrogen atoms at the double bond in cyclohexene to 4.2–3.8 ppm instead of 6.8 ppm in the noncoordinated olefin and decrease by 75–100 cm⁻¹ of the stretching vibration frequency of the double bond indicate coordination of the alkene with the transition metal and agree with published data [7, 8]. The IR spectra of the resulting compounds contain a system of five (for chromium-subgroup metals) or four (for Fe) well-resolved bands in the range 1900–2100 cm⁻¹, which indicates that only one CO molecule is substituted by cyclohexene.

The resulting organometallic compounds react with dialkyl hydrogen phosphites on mixing of a solution of the π complex in benzene or alkene with an equimolar amount of dialkyl hydrogen phosphite and a catalytic amount of triethylamine. We performed reactions of cyclohexene π complexes with dialkyl hydrogen phosphites under conditions considerably milder than those of the classical Pudovik reaction, as in the alcohol–alcoholate medium the coordinated double bond undergoes hydrogenation, with decomposition of the organometallic compound [6].

After keeping the reaction mixtures of π -complexes with dialkyl hydrogen phosphites for 2–3 days at room temperature, new singlet signals appear in the ³¹P NMR spectra, shifted downfield relative to the signals of the initial dialkyl hydrogen phosphites: δ_p 32 and 27.6 ppm for the systems with dimethyl and diethyl hydrogen phosphites, respectively. The chemical shifts of the new signals depend only on the structure of the initial dialkyl hydrogen phosphite and are independent of the nature of the transition metal, which suggests formation of the same product in reactions of the same dialkyl hydrogen phosphite with different π complexes.

From the mixture formed in reaction of dimethyl hydrogen phosphite with η^2 -(cyclohexene)tetracarbonyliron(0), we isolated dimethyl cyclohexylphosphonate **I**, which was identified by elemental analysis and ¹H and ³¹P NMR spectroscopy. The ¹H signal at δ 1.17 ppm (J_{HP} 17.4 Hz) belongs to the methine group in the cyclohexyl ring, bound to phosphorus; the signal at 3.50 ppm (J_{HP} 11.7 Hz) belongs to the methoxy groups; low-field signals characteristic of hydrogen atoms at the C=C bond are absent. The ³¹P signal at δ_P 32 ppm is typical for alkylphosphonates. The IR spectrum contains a broad band at 1250 cm⁻¹ [v(P=O)] and a strong narrow band at 1025 cm⁻¹



R = Me (I), Et (II); $M(CO)_x = Fe(CO)_4$, $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$; x = 4 (M = Fe), 5 (M = Cr, Mo, W).

The intensity ratio of the phosphonate and dialkyl hydrogen phosphite signals in the ³¹P NMR spectra corresponds to the 20–70% yield of phosphonates **I** and **II** based on the metal complex. With the same π complexes and under similar conditions, dimethyl cyclohexylphosphonate is formed in a higher yield than the diethyl derivative [e.g., 75 and 63%, respectively, in the case of η^2 -(cyclohexene)tetracarbonyl-iron(0)]. Heating or refluxing of the reaction mixtures accelerates formation of phosphonates.

Solid crystalline products isolated from the reaction mixtures are degradation products of metal carbonyl complexes (probably polynuclear complexes). The IR spectra of these compounds contain only ill-resolved bands in the range $1900-2100 \text{ cm}^{-1}$.

We assumed that phosphorylation of the olefin complex and release of the phosphonate result in generation of a coordination-unsaturated 16-electron species $Fe(CO)_4$ or $M(CO)_5$ (M = Cr, Mo, W), capable of further complexation. Therefore, it should be possible to perform addition of dialkyl hydrogen phosphites to cyclohexene or 1-hexene, catalyzed by $Fe(CO)_5$ or $M(CO)_6$ (M = Cr, Mo, W). Indeed, in a mixture containing alkene, dialkyl hydrogen phosphite, triethylamine, and metal carbonyl, we also observed formation of dialkyl alkylphosphonates identical to those prepared by the stoichiometric reaction of the alkene π Yields of dialkyl cyclohexylphosphonates in reaction of cyclohexene with dialkyl hydrogen phosphites in the presence of $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO_6$, or $W(CO)_6$ and triethylamine^a

	Metal complex	Yield, %	
(RO) ₂ P(O)H		based on metal complex	based on (RO) ₂ P(O)H
(MeO) ₂ P(O)H	Fe(CO) ₅	240	24
-	Cr(CO) ₆	300	30
	Mo(CO) ₆	53	5
	W(CO) ₆	290	29
(EtO) ₂ P(O)H	$Fe(CO)_5$	200	20
-	$Cr(CO)_{6}$	275	28
	Mo(CO) ₆	46	5
	W(CO) ₆	250	25
(i-PrO)2P(O)H	$Fe(CO)_5$	160	16
	W(CO) ₆	220	22

^a Cyclohexene (48 mmol), dialkyl hydrogen phosphite (12 mmol), metal complex (1.2 mmol), and triethylamine (0.2 mmol) were refluxed for 5 h under argon. The yields were determined by 31 P NMR spectroscopy.

complex with dialkyl hydrogen phosphite. The yields of cyclohexylphosphonates obtained at the molar ratio metal complex : dialkyl hydrogen phosphite 1 : 10 with various metal complexes and dialkyl hydrogen phosphites are listed in the table.

It should be noted that the yield of dialkyl cyclohexylphosphonates decreases in going from dimethyl to diisopropyl esters under equal other conditions. This fact is an evidence in favor of the ionic mechanism of the catalytic addition, because in the case of radical addition of hydrophosphoryl compounds to alkenes the reactivity tends to increase with increasing size of the alkyl substituent [1, 2], which is due to increase in the chain transfer constant of the radical reaction.

The catalytic effect of $Cr(CO)_6$ and $W(CO)_6$ is approximately equal and is slightly stronger than that of Fe(CO)₅. This trend may be due to the fact that, although the iron carbonyl π complexes are more stable than those of Cr, Mo, and W, the latter complexes are more labile and under conditions of thermochemical activation are formed faster than the corresponding iron complexes. The lowest yield observed with Mo(CO)₆ is apparently due to the lowest, as compared to Cr and W, stability of Mo(CO)₆ and molybdenum carbonyl π complexes and their increased tendency to thermochemical degradation [9].

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Addition of dialkyl hydrogen phosphite to 1-hexene occurs probably according to and against the Markownikoff rule. Formation of an isomeric mixture is suggested by the presence of two closely located singlets in the ³¹P NMR spectrum of the reaction mixture 1-hexene–dimethyl hydrogen phosphite– $Cr(CO)_6$ -triethylamine after refluxing for 3 h (δ_P 34 and 36 ppm, ratio 3 : 1, respectively).

In the absence of the amine, addition of dialkyl hydrogen phosphite to cyclohexene with Fe(CO)₅ catalyst under conditions given in the table does not occur or occurs to an extremely low extent (10–15% based on the metal complex). The decisive role of the amine, on the one hand, suggests the ionic mechanism of the catalytic reaction. On the other hand, the presence of the amine in the reaction mixture is necessary for accelerating formation of the π complex [7]. Thus, the loss of the catalytic activity in the absence of the amine may be due to decelerated formation of π complexes.

It was noted in [3, 4] that the key stage of the catalytic addition of dialkyl hydrogen phosphites to alkenes and alkynes in the presence of Pd(0) and Pt(0) complexes is oxidative addition of the P–H bond to the transition metal. To make a substantiated conclusion on the mechanism of the reaction in question, we studied the reaction of the metal carbonyls with dialkyl hydrogen phosphites.

The reaction of dimethyl and diethyl hydrogen phosphites with $W(CO)_6$ or $Fe(CO)_5$ does not occur to a noticeable extent when the solution of the metal carbonyl in the phosphite is stored at room temperature or at prolonged heating of a hexane solution of dialkyl hydrogen phosphite and metal carbonyl (molar ratio 10:1). On refluxing of solutions of Fe(CO)₅ and $W(CO)_6$ in dialkyl hydrogen phosphite (molar ratio phosphite : metal 22 : 1), the solution color changes from colorless to dark violet [solution of $W(CO)_6$ in $(EtO)_2P(O)H$ or from pale orange to purple [mixture of Fe(CO)₅ and (EtO)₂P(O)H]. The solutions remained homogeneous and did not change the appearance for several days at room temperature under argon. We failed to find conditions for isolating the product of reaction of dialkyl hydrogen phosphite with the metal carbonyl complex (adducts IIIa and IIIb). On attempted distillation of excess dialkyl hydrogen phosphite in a water-jet-pump or roughingpump vacuum, the solution became heterogeneous [formation of a solid phase in the case of $W(CO)_6$ or of a tar in the case of $Fe(CO)_5$]. The bottom residue after removal of dialkyl hydrogen phosphite, according to the IR data, consists of polycarbonyl complexes of Fe or W. The low solubility of the bottoms from

the $W(CO)_6$ -(EtO)_2P(O)H mixture and the strong paramagnetic broadening of the signals in the case of the Fe(CO)_5-(EtO)_2P(O)H mixture did not allow us to interpret the ³¹P NMR spectra of substances obtained after distillation of excess dialkyl hydrogen phosphite. Probably, our failure to isolate adducts **IIIa** and **IIIb** may be due to their existence only in equilibrium with free dialkyl hydrogen phosphites and to their irreversible decomposition when excess phosphite is removed.

The ³¹P NMR spectrum of the mixture prepared by reaction of diethyl hydrogen phosphite with W(CO)₆ suggests formation of a new organophosphorus compound. Along with the signal from diethyl hydrogen phosphite (δ_P 9 ppm, J_{PH} 680 Hz), the spectrum contains a well-defined signal at δ_P 6.2 ppm with a coupling constant of 353 Hz (determined from satellite splitting), suggesting the presence of a four-coordinate phosphorus atom covalently bonded to W in **IIIb**:

$$M(CO)_{x} + (EtO)_{2}P(O)H \longrightarrow [M]-P(OEt)_{2},$$

IIIa, IIIb

$$M = Fe, x = 5$$
 (a); $M = W, x = 6$ (b).

The satellite splitting with *J* 353 Hz is well consistent with published data on the first-order coupling constants ¹⁸³W–P [10, 11]. The intensity ratio of the major and satellite signals is also consistent with the natural abundance (14 at. %) of the isotope ¹⁸³W responsible for the satellite splitting. The preservation of the valence and coordination number of phosphorus in IIIb is suggested by insignificant change of the ³¹P chemical shift relative to diethyl hydrogen phosphite. Experimental data and results of quantum-chemical calculations in [12] show that the group electronegativity and chemical shielding effect of W(0) are practically equal to those of the hydrogen atom.

Unfortunately, available data do not allow more accurate description of the structure of IIIa and IIIb and any assumptions concerning the pathway of their formation from metal carbonyls and dialkyl hydrogen phosphites.

Mixing of cyclohexene with a solution of **IIIb** in diethyl hydrogen phosphite at room temperature results in a vigorous reaction. The process is strongly exothermic, the solution color after mixing changes from dark violet to pale green, and a precipitate is formed, consisting, according to the IR spectrum, of polynuclear W(0) carbonyl complexes with traces of phosphoryl-containing fragments. From the solution, after separation of the precipitate, we isolated diethyl

cyclohexylphosphonate (yield 80%), which was identified by the ¹H and ³¹P NMR spectra ($\delta_{\rm p}$ 27 ppm; δ 1.22 ppm, $J_{\rm PH}$ 16.8 Hz, methine proton). The most probable pathway of phosphonate formation is insertion of the alkene double bond into the P–M bond (similarly to [3]).

$$\bigcirc \xrightarrow{\text{IIIb}} \text{II}.$$

It should be noted, however, that, when addition of dialkyl hydrogen phosphites to alkenes is performed in the presence of homoligand carbonyl complexes of transition metals, the addition mechanism can be different. Thus, the signals of IIIa and IIIb are not observed in the ¹³P NMR spectra of the reaction mixtures η^2 -(alkene)M(CO)_x–(RO)₂P(O)H–NEt₃ and M(CO)_x–alkene–(RO)₂P(O)H–NEt₃.

In our opinion, the procedure involving preliminary activation of dialkyl hydrogen phosphite by reaction with the metal (formation of the M–P bond) followed by reaction of the alkene with the M–P bond is preferable.

EXPERIMENTAL

The IR spectra were taken on a Specord M-80 spectrophotometer (mulls in mineral oil). The ¹H NMR spectra were recorded on Varian Unity-300 (298.4 MHz), Bruker-100 (100 MHz), and Bruker Gemini-200 (199.827 MHz) spectrometers at 25°C; the chemical shift was determined relative to the signals of the residual protons of the solvents (C_6D_6 , CDCl₃, CD₃OD); the solution concentration was 0.7–1.5 wt %. The ³¹P NMR spectra were recorded on Varian Unity-300 (121.4 MHz) and RYa-2303 (8 MHz) spectrometers, with 85% H₃PO₄ as external reference.

All manipulations were performed under argon.

 $η^2$ -(Cyclohexene)pentacarbonyltungsten(0). A solution of 0.5 g of W(CO)₆ in a mixture of 4 ml of THF and 4 ml of cyclohexene was irradiated with UV light from a high-pressure mercury lamp for 5–6 h with continuous stirring. After irradiation completion, the mixture was concentrated by removing the solvent in a water-jet-pump vacuum to a volume of 1.5– 2.0 ml, and the precipitate was filtered off. A finely crystalline light yellow powder was obtained, yield 46%, decomposition point 78–82°C. IR spectrum, v, cm⁻¹: 1510 (coordinated C=C bond); 1990, 1970, 1940, 1920, 1900 (coordinated CO ligands). ¹H NMR spectrum, δ, ppm: 4.1 m, 3.8 m (coordinated CH=CH bond). $η^2$ -(Cyclohexene)pentacarbonylchromium(0), η^2 -(cyclohexene)pentacarbonylmolybdenum(0), η^2 -(cyclohexene)tetracarbonyliron(0), η^2 -(1-hexene)pentacarbonylchromium(0), η^2 -(1-hexene)pentacarbonylmolybdenum(0), η^2 -(1-hexene)tetracarbonyliron(0), and η^2 -(1-hexene)pentacarbonyltungsten(0) were prepared similarly. The complexes of Cr, Mo, and W can be prepared not only by UV irradiation of reaction mixtures for 5 h, but also by their refluxing for 3–4 h.

Reaction of dialkyl hydrogen phosphites with η^2 -(cyclohexene)pentacarbonyltungsten(0). To a solution of 0.5 g of η^2 -(cyclohexene)pentacarbonyltungsten(0) in 8 ml of cyclohexene we added 0.15 ml of dimethyl hydrogen phosphite. The mixture was allowed to stand at room temperature for several days or refluxed for 30-45 min, after which it was concentrated in a water-jet-pump vacuum. The crystals that formed were filtered off, and the filtrate was concentrated to constant volume (~0.08 ml). The residue, a viscous liquid (dimethyl cyclohexylphosphonate, I), was vacuum-distilled; bp 190-210°C (10 mm Hg). IR spectrum, v, cm⁻¹: 1250 (P=O), 1025 narrow, s (P–O–CH₃). ¹H NMR spectrum, δ , ppm: 1.17 d (J_{HP} 17.4 Hz, methine group in the cyclohexyl ring, bound to phosphorus), 3.50 m (J_{HP} 11.7 Hz, O-methyl groups bound to phosphorus); low-field signals characteristic of hydrogen atoms at the C=C bond are absent. ³¹P NMR spectrum, δ_{P} , ppm: 32 s (typical for phosphorus atoms in alkylphosphonates). Found P, %: 16.3. C₈H₁₇O₃P. Calculated P, %: 16.1.

The reactions with the other combinations of dialkyl hydrogen phosphites and cyclohexene π complexes of transition metals were performed similarly.

Catalytic reaction of diethyl hydrogen phosphite with cyclohexene in the presence of W(CO)₆. A mixture of 0.42 g of W(CO)₆, 10 ml of cyclohexene, and 1-2 drops of triethylamine was refluxed for 1 h, 1.0-1.5 ml of diethyl hydrogen phosphite was added, and the mixture was refluxed for an additional 3–5 h. Then the mixture was concentrated in a water-jetpump vacuum. The crystalline products were filtered off, and the filtrate was distilled in a water-jet-pump vacuum or high vacuum. Certain amount of unchanged diethyl hydrogen phosphite was recovered, and diethyl cyclohexylphosphonate II, bp 195–220°C (8 mm), was isolated. IR spectrum (thin film), v, cm⁻¹: 1230 (P=O), 1040 narrow, s (P–O–CH₂). ¹H NMR spectrum, δ , ppm: 1.23 d (J_{HP} 17.1 Hz, methine group in the cyclohexyl ring bound to phosphorus), 3.80 m ($J_{\rm HP}$ 12.0 Hz, O-methylene groups bound to phosphorus); low-field signals characteristic of hydrogen atoms at C=C bond are absent. ³¹P NMR spectrum, δ_{P} , ppm: 27.8 s. Found P, %: 14.15. $C_{10}H_{21}O_{3}P$. Calculated P, %: 14.06.

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Reactions with the other combinations of olefin cyclohexene, 1-hexene), dialkyl hydrogen phosphite (dimethyl, diethyl, diisopropyl), and metal carbonyl $[Cr(CO)_6, Mo(CO)_6, Fe(CO)_5]$ were performed similarly.

Reaction of diethyl hydrogen phosphite with $W(CO)_6$. A mixture of 0.5 g of $W(CO)_6$ and 4 ml of diethyl hydrogen phosphite was refluxed for 3 h. ³¹P NMR spectrum of the reaction mixture, δ_{P} , ppm: 6.2 (J_{PW} 353 Hz, from satellite splitting $P^{r_1 g_3 r}_{-1 g_3 W}$). To the resulting solution we added 3 ml of cyclohexene and 1–2 drops of triethylamine at room temperature. A vigorous exothermic reaction was observed. The crystalline products were filtered off, and the filtrate was distilled. A certain amount of unchanged diethyl hydrogen phosphite was recovered, and diethyl cyclohexylphosphonate II was obtained, bp 175-180°C (5 mm Hg). IR spectrum (thin film), v, cm⁻¹: 1230 (P=O), 1025 narrow, s (P-O-CH₃). ¹H NMR spectrum, δ , ppm: 1.21 d (J_{HP} 16.9 Hz, methine group in the cyclohexyl ring bound to phosphorus), 3.47 $(J_{\rm HP}$ 11.8 Hz, O-methylene groups bound to phosphorus); the low-field signals characteristic of hydro-gen atoms at C=C bond are absent. ³¹P NMR spectrum, $\delta_{\mathbf{P}}$, ppm: 27.6 s (typical of the phosphorus atoms in alkylphosphonates). Found P, %: 13.95. $C_{10}H_{21}O_3P$. Calculated P, %: 14.05.

ACKNOWLEDGMENTS

The study was financially supported by the Ministry of Education of the Russian Federation, General and Technical Chemistry program.

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