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> SHORT COMMUNICATIONS

Synthesis of Dimethyl Phenylphosphonates Catalyzed by Group VI Metal(0) Hexacarbonyls

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Abstract—The coupling of dimethyl phosphite and iodobenzene occurs in the presence of catalytic amounts of homoligand carbonyl complexes of chromium subgroup metals to form dimethyl phenylphosphonate in yields of 50–73% depending on the metal.

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Organophosphorus compounds attract attention due to their broad-range potential practical [1]. Arylphosphonates can serve as intermediates in the synthesis of functionalized organophosphorus compounds [2] and can be used as pharmacologically active compounds [3]. The use of arylphosphonates in the design of new materials has been reported [4]. They have also been used as organoelement catalysts [5]. A lot of catalytic syntheses of organophosphorus compounds, including those from hydrocarbons, are known [6].

P-Arylation allows synthesis of aromatic organophosphorus compounds, first of all arylphosphines, which are the most common ligands in transition metal complex catalysts [7]. There is a present tendency to replace Pt and Pd catalysts of P–C bond-forming reactions [8] by derivatives of less costly metals, specifically copper [9, 10]. The stoichiometric dechlorophosphorylation of chlorobenzene incorporated in the (η^6 -C₆H₅Cl)Cr(CO)₃ complex [11]; the resulting diethyl phenylphosphonate does not leave the coordination sphere of chromium.

In view of the fact that arenetricarbonyl complexes of chromium subgroup metals can form be formed upon refluxing solutions of metal(0) hexacarbonyls in high-boiling arenes [12], we reacted dimethyl phosphite with the (η^6 -C₆H₅I)Cr(CO)₃ complex formed *in situ* from chromium(0) hexacarbonyl in iodobenzene under reflux, in the presence of trimethylamine (the organometallic compound, dimethyl phosphite, and trimethylamine were taken in a 1 : 1.2 : 1.2 molar ratio). According to the ³¹P NMR data, a complete conversion of dimethyl phosphite took place. The ³¹P NMR spectrum of the reaction mixture displayed a single signal at δ 22.7 ppm, which, according to published data [13], was signed to phosphorus in dimethyl phenylphosphonate. Apparently, dimethyl phenylphosphonate that forms leaves the coordination sphere of chromium, while chromium(0) hexacarbonyl or its transformation product catalyzes formation of dimethyl phenylphosphonate.

To find evidence for this suggestion, we synthesized dimethyl phenylphosphonate by reacting iodobenzene with dimethyl phosphite in the presence of catalytic amounts of chromium hexacarbonyl and other homocarbonyl Group VI metal complexes (Mo, W).

With all the three metal hexacarbonyls, the ³¹P NMR spectra of the reaction mixtures showed signals of the main reaction product, an organophosphorus compound which gives a singlet at δ 22.7 ppm. In the case of Cr(CO)₆, the reaction product, dimethyl phosphonate **1**, could be isolated (see scheme).



The ¹H NMR spectrum of compound **1** displays doublets at δ 3.78 ppm, ³*J*(P,OCH₃) 11.0 Hz, assignable to methoxyl protons, and a multiplet at 7.40–7.80 ppm, assignable to phenyl protons. In the ¹³C NMR spectra, the signals of these groups are observed at δ 53 and 127–139 ppm, respectively. The boiling point and refractive index of the isolated compound, as well as its ³¹P NMR chemical shift are consistent with those reported in [13] for dimethyl phenylphosphonate. The elemental analysis of compound **1**, too, is consistent with the proposed structure.

According to the 31 P NMR data, Group VI metal carbonyl complexes differ in the efficiency to catalyze the iodoarene deiodophosphorylation reaction. Under the same reaction conditions, the replacement of Cr(CO)₆ by W(CO)₆ decreases the conversion of dimethyl phosphite and the yield of dimethyl phenylphosphonate (see table).

We explain the decrease of the catalytic activity of the M(CO)₆ complexes with increasing charge of the metal by the decreasing rate of formation of arenetricarbonyl complexes in the reaction of arene with metal hexacarbonyl in the series chromium>molybdenum>tungsten [14]. Presumably, the activity of the discovered catalytic system is controlled by the rate of formation of the (η^6 -C₆H₅I)M(CO)₃ complexes in the PhI–M(CO)₆ system. As known, the (η^6 -ArX)M(CO)₃ complexes undergo a rather facile nucleophilic substitution of halogen by the S_NAr mechanism [8, 15].

Further, we are going to study the mechanism of the discovered catalytic reaction in more detail and expand its synthetic potential by involving in this catalytic coupling other hydrophosphoryl compounds and iodoarenes.

Commercial dimethyl phoshite and iodobenzene were purified by standard procedures. Commercial metal(0) hexacarbonyls were purified by vacuum sublimation (5×10^{-2} mmHg) at 60–80°C.

Dimethyl phenylphosphonate (1). *a.* Iodobenze, 2.25 mL (20 mmol), dimethyl phosphite, 1.8 mL (20 mmol), trimethylamine, 2.8 mL (20 mmol), and 2 mmol of metal(0) hexacarbonyl [0.44 g Cr(CO)₆, 0.53 g Mo(CO)₆, or 0.70 g W(CO)₆] were placed into a 10-mL flask. The resulting mixture was refluxed for 5 h and then analyzed by ³¹P NMR spectroscopy. ³¹P

Conversions of dimethyl phosphite and yields of dimethyl phenylphosphonate in Group VI metal complex-catalyzed reactions (³¹P NMR data)

	Conversion of	Yield of dimethyl
Catalyst	dimethyl phosphite,	phenylphosphonate 1,
	%	%
$Cr(CO)_6$	100	96
Mo(CO) ₆	74	56
$W(CO)_6$	57	50

NMR spectrum (C₆D₆), δ , ppm: 11.0 d [(CH₃)P(O)H, ¹J_{PH} 693 Hz], 22.7 s [(CH₃)P(O)Ph].

b. Iodobenze, 11.25 mL (0.1 mol), dimethyl phosphite, 9.0 mL (0.1 mol), trimethylamine, 14.0 mL (0.1 mol), and 2.2 g (0.01 mol) of chromium(0) hexacarbonyl were placed into a 50-mL flask. The resulting mixture was refluxed for 5 h, and then worked up to isolate dimethyl phenylphosphonate, yield 13.6 g (73%). The physical and physicochemical characteristics of the product were identical to those in [13].

The ¹H NMR spectra were measured on a Bruker Avance III 400 instrument (400.0 MHz) in deuterobenzene- d_6 ; the chemical shifts were measured against residual proton signals of the deuterated solvent. The ³¹P NMR spectra were run on a Bruker Avance III 400 spectrometer (161.9 MHz), external reference 85% aqueous H₃PO₄. The ¹³C NMR spectra were obtained on a Bruker Avance III 400 spectrometer (100.4 MHz), internal reference deuterobenzene- d_6 .

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