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Regio- and stereospecific hydrophosphorylation of phenylacetylene

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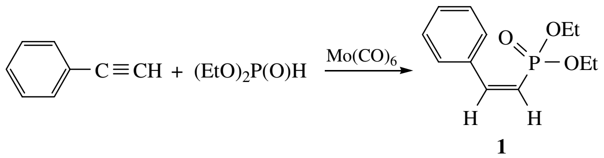
The interaction of diethyl phosphite with phenylacetylene within the coordination sphere of the trialkynemonocarbonylmolybdenum(0) complex produces diethyl (*Z*)-2-phenylvinylphosphonate.

The attractiveness of the catalytic phosphorylation[1] and phosphination[2] of alkenes and alkynes can be described not only by an acceleration of the formation of target organophosphorus compounds but also by the fact that the use of homogeneous catalysis with transition metals can produce organophosphorus compounds that cannot be obtained under conditions of classic organoelement synthesis. We reported the addition of dialkyl phosphites to alkenes in the presence of chromium-group metal carbonyl complexes[3] and the dehalophosphorylation of chloro- and bromobenzene in the coordination sphere of the aryltricarbonyl complexes of the above metals.[4]

Here we describe the addition of diethylphosphite to phenylacetylene in the presence of hexacarbonylmolybdenum(0). The hydrophosphorylation of the alkyne proceeds under the refluxing of a reaction mixture containing stoichiometric quantities of phenylacetylene and diethyl phosphite in the presence of 10 mol% $Mo(CO)_6$ as a catalyst in an atmosphere of dry argon. The addition of dialkylphosphites proceeds as a regio- and stereospecific process with the quantitative formation of a single organophosphorus product – an internal vinylphosphonate with the *cis*-disposition of hydrogen atoms relatively to the double bond – *O*,*O*-diethyl-(*Z*)-2-phenylvinylphosphonate **1**.

The composition and structure of phosphonate **1** were studied by mass spectrometry, elemental analysis, and IR, ^{1}H and ^{31}P NMR spectroscopy.[†]



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In order to explain the regio- and stereospecificity of phenylacetylene hydrophosphorylation, the structure of the catalytically active intermediate of the addition reaction was studied. The fractional recrystallization of the reaction mixture allowed us to isolate organometallic compound **2**, which is characterised as monocarbonyltri(phenylacetylene)molybdenum(0) using elemental analysis, IR[‡] and ^{1}H NMR spectroscopy.

In the ^{1}H NMR spectra of compound **2**, the acetylenic hydrogen atom displays the singlet upfield chemical shift (1.64 ppm in

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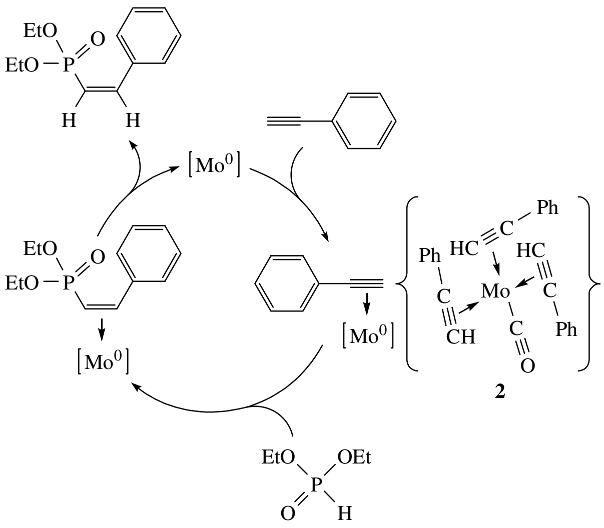
[†] For **1**: ^{1}H NMR, δ: 7.95 (d, 1H, PhC*H*=, $^3J_{\text{HH-cis}}$ 8.35 Hz), 6.50 (dd, 1H, =CHP, $^2J_{\text{HP}}$ 29.5 Hz, $^3J_{\text{HH-cis}}$ 8.35 Hz), 7.00–7.65 (m, 5H, Ph), 3.74 (q, 4H, 2OCH_2Me), 1.27 (t, 6H, 2OCH_2*Me*). ^{31}P NMR, δ: 2.56 (s). IR (ν/cm^{-1}): 1210 (P=O), 1650 (Ph), 1700 (C=C). MS, *m*/*z*: 240.1 (M$^+$). Found (%): C, 60.05; H, 7.15; P, 12.75. Calc. for $C_{12}H_{17}O_3P$ (%): C, 59.99; H, 7.13; P, 12.89.

[‡] For **2**: IR (ν/cm^{-1}): 2036 (C=O). Found (%): C, 70.33; H, 4.15. Calc. for $C_{25}H_{18}MoO$ (%): C, 69.77; H, 4.22.



2

compound **2**, 3.06 ppm in non-coordinated phenylacetylene). The spectral characteristics of organometallic compound **2** are in good agreement with previously reported data on an analogous triphenylacetylene tungsten complex.[5] Note that the monocarbonyl complexes of zero-valent chromium-group metals having three molecules of phenyl- and diphenylacetylene earlier were produced only from tricarbonyltrinitrile or benzyltricarbonyl molybdenum and tungsten complexes.[6] Thus, we observed the first example of the formation of the (alkyne)$_3$Mo(CO) complex *via* the direct interaction of an alkyne with hexacarbonylmolydenum(0).

Organometallic compound **2** is an intermediate in the catalytic hydrophosphorylation of phenylacetylene to form *O*,*O*-diethyl-(*Z*)-2-phenylvinylphosphonate.

The entrance of phenylacetylene to the molybdenum coordination sphere reduces the electronic density on the triple bond. This facilitates a nucleophilic attack of the hydrophosphoryl compound. The primary attack of the P-nucleophile is directed towards the terminal carbon atom of the triple bond. It is caused by the steric hindrance of the triple bond carbon atom connected with the phenyl ring. The terminal carbon atom of the phenylacetylene triple bond is most electrophilic.

The addition of a phosphoryl group probably leads to the weakening of the *O*,*O*-diethyl-(*Z*)-2-phenylvinylphosphonate bond with the metal core and to phosphonate dissociation from the coordination sphere. The coordinatively unsaturated organometallics can be bound with another phenylacetylene molecule, closing a catalytic cycle. The stereospecificity of the P–H fragment addition can be caused by the template effect of transition metal atoms.

The proposed mechanism can be proved both by the regiochemistry of the reaction and by the absence of bis(phosphonates) – the products of the addition of dialkylphosphites to vinylphosphonates in the final reaction mixture. The previously reported examples of dialkylphosphites towards alkynes, proceeding through the interaction of organophosphorus compounds with transition metal complexes either proceed according to the Markovnikoff rule[7] or do not stop on the formation of the monophosphonate, producing bis(phosphonates) independently from the alkyne : diethylphosphite ratio.[8]

The above regio- and stereospecific addition of dialkyl phosphite to phenylacetylene in the coordination sphere of molybdenum(0) opens up new opportunities to the use of chromium-group organometallic compounds in the directed synthesis of organophosphorus compounds.

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