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From Furans to Phosphinines

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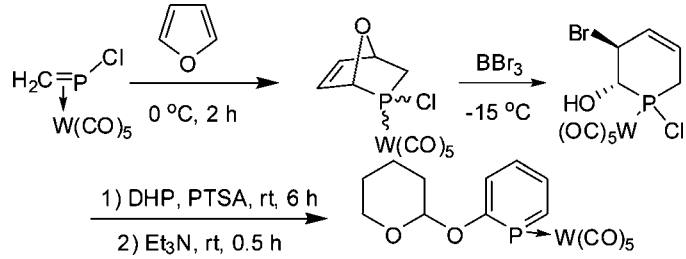
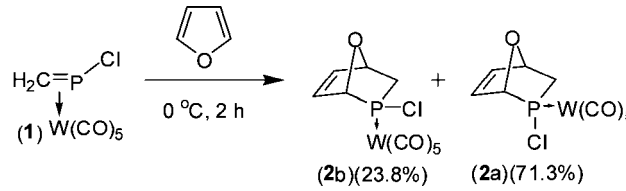
ABSTRACT



The reaction between methylenechlorophosphine-pentacarbonyltungsten and furan affords a [4 + 2] adduct whose oxygen bridge is broken by BBr_3, leading to a 2-alkoxyphosphinine after two additional steps.

Phosphinines play a central role in phosphorus heterocyclic chemistry because they are the simplest aromatic species in the field and are among the most efficient ligands for the rhodium-catalyzed hydroformylation of olefins.[1] Thus, there is a constant need for new versatile synthetic methods allowing tuning of their electronic and steric properties. Many such methods have been described,[2] but none uses one of the fundamental heterocycles as a starting point. Such a conversion would drastically increase the availability of phosphinines. To put things in perspective, the Chemical Abstracts data bank contains 1 715 000 entries related to furan and its derivatives and only 2800 entries dealing with phosphinines. We describe hereafter a route converting furans into phosphinines. Some time ago, we synthesized methylenechlorophosphine as a stable but reactive pentacarbonyltungsten complex.[3] This species easily reacts with furan at 0 °C to give almost quantitatively the [4 + 2] cycloadduct **2** as a mixture of two isomers (Scheme 1). The major one

Scheme 1. Cycloaddition of Methylenechlorophosphine-pentacarbonyltungsten and Furan



(**2**a) has the tungsten in the *exo* position as shown by the X-ray crystal structure analysis (Figure 1).

Upon reaction with boron tribromide in the cold, the oxygen bridge of **2** is quantitatively cleaved to give **3**. Two pieces of information establish its structure. The OH appears as a doublet of doublets at 2.95 ppm in $CDCl_3$ with a J_{HP} coupling of 27.9 Hz. Also, the C*H*OH is strongly correlated with the CHBr proton (COSY). The stereochemistry is only tentative. Attempted direct dehydrohalogenation of **3** by Et_3N in the presence of Me_3SiCl unexpectedly led to the ring-expanded product (**4**) whose structure was established by X-ray analysis (Figure 2).

It was thus necessary to protect the OH group to prevent the ring expansion. This was done using dihydropyran. The

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(2) Mathey, F.; Le Floch, P. *Sci. Synth.* **2005**, *15*, 1097.

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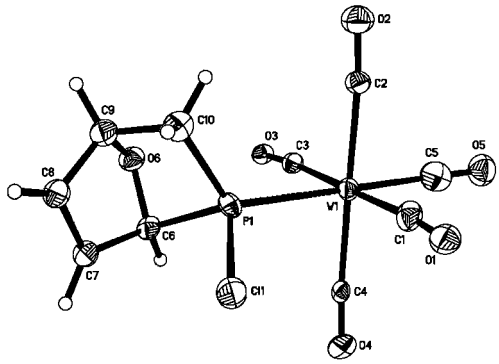


Figure 1. X-ray structure of **2**a.

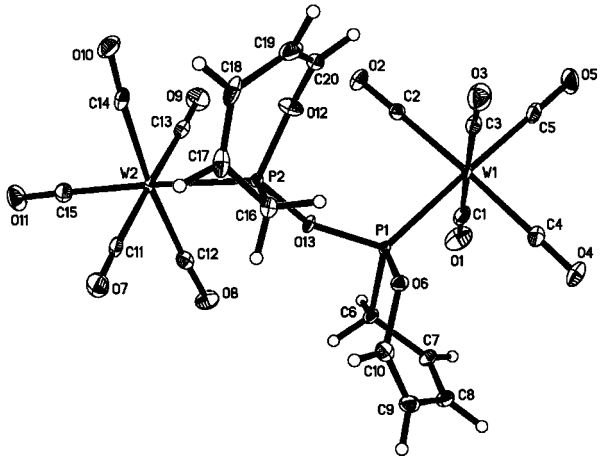
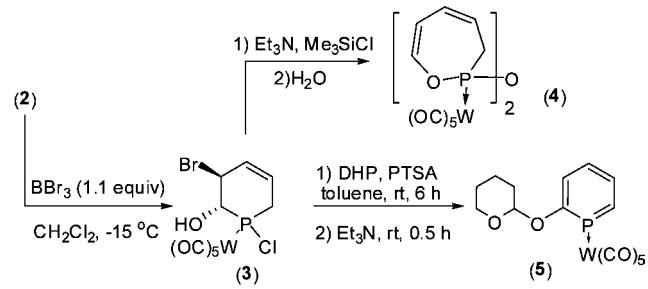


Figure 2. X-ray structure of **4**.

resulting protected product was then smoothly dehydrohalogenated by triethylamine to give the expected 2-alkoxyphosphinine complex **5** (Scheme 2).

Scheme 2. Conversion of the [4 + 2] Cycloadducts into Phosphinine



The phosphinine[4] was purified by chromatography on Al_2O_3 at −6 °C. The overall yield of phosphinine from furan is ca. 60%. In view of the very mild conditions used throughout this scheme, we expect a rather broad usefulness.

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Supporting Information Available: Experimental section and X-ray data for **2**a and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) **5**: ^{31}P NMR ($CDCl_3$) δ 138.2, $^1J_{PW}$ = 262.4 Hz; ^{1}H NMR ($CDCl_3$) δ 1.46−2.30 (m, 6H, CH_2), 3.69 (m, 1H, OCH_2), 3.88 (m, 1H, OCH_2), 5.63 (br., 1H, OCHO), 7.39 (m, 1H, =CH), 7.51 (m, 1H, =CH), 7.75 (dd, J = 12.4 and 9.2 Hz, 1H, =CH), 8.31 (ddd, $^1J_{HP}$ = 26.4 Hz, $^3J_{HH}$ = 9.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, =CH-P); ^{13}C NMR ($CDCl_3$) δ 17.96 (s, CH_2), 24.92 (s, CH_2), 29.84 (s, CH_2), 61.85 (s, OCH_2), 97.93 (d, J_{CP} = 7 Hz, OCHO), 122.15 (d, J_{CP} = 3 Hz, =CH), 128.96 (d, J_{CP} = 25 Hz, =CH), 131.06 (d, J_{CP} = 19 Hz, =CH), 150.60 (d, $^1J_{CP}$ = 22 Hz, =CH−P), 181.61 (d, $^1J_{CP}$ = 44 Hz, =C−P), 194.44 (d, $^2J_{CP}$ = 9 Hz, *cis*-CO), 199.25 (d, $^2J_{CP}$ = 31 Hz, *trans*-CO).