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The Phospha-Cope Rearrangement of 4^{λ}-Phospha-1-hexen-5-yne Derivatives

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The title compounds (**1**) were refluxed in hexanol to give the corresponding 1,4-pentadienylphosphinates, which seem to be formed via transient "phospha-allene derivatives", together with Michael adducts of alcohol to the triple bond of **1**.

In a previous paper,[1] we reported on the phospha-Cope rearrangement of 3^{λ}-phospha-1,5-hexadiene derivatives. On the other hand, the Cope-rearrangements of 1-hexen-5-yne derivatives involving a hetero atom have been utilized to synthesize the corresponding cumulenes such as allene,[2] thioketene,[3] and selenoketene.[4]

In this paper we wish to report that 4^{λ}-phospha-1-hexen-5-yne derivatives may undergo a similar rearrangement to give "phospha-allene derivatives", which can be trapped by alcohol to afford the corresponding 1,4-pentadienylphosphinates.

4-Phenyl- and 1,6-diphenyl-4^{λ}-phospha-1-hexen-5-yne 4-oxides (**1a** and **1b**) were prepared by reactions of allylphenylphosphinyl chloride with ethynylmagnesium bromide and 2-phenylethynyllithium in 68 and 35% yields, respectively. The corresponding sulfides (**1c** and **1d**) were obtained by sulfurization of **1a** and **1b** with Lawesson's reagent in 51 and 97% yields, respectively.

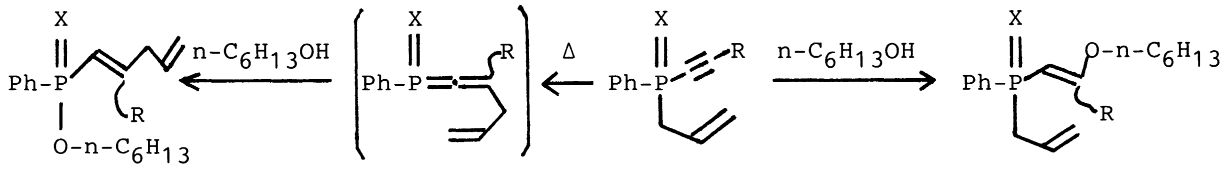
The oxides **1a,b** were refluxed in hexanol to give a mixture of the corresponding hexyl E- and Z-(1,4-pentadienyl)phenylphosphinates (E,Z-**3a,b**) and E- and Z-1-hexyloxy-3-phenyl-3^{λ}-phospha-1,5-hexadiene 3-oxides (E,Z-**4a,b**), while the reaction of the sulfides **1c,d** afforded only O-hexyl E- and Z-(1,4-pentadienyl)phenylphosphinothioates (E,Z-**3c,d**). The results are shown in Table 1.

Table 1. Reaction products from **1a-d**

1	Time/h	Product[a]	Yield/%	**1**	Time/h	Product	Yield/%
a: X=O; R=H	2	**3a**	90 (10:1)[b]	**c**: X=S; R=H	2	**3c**	87 (15:1)
		4a	8 (7:1)				
b: X=O; R=Ph	60	**3b**	50 (1:1)	**d**: X=S; R=Ph	50	**3d**[c]	95 (1:1)
		4b	50 (1:1)				

a) The products gave satisfactory ^{1}H-, ^{13}C-, and ^{31}P-NMR ($CDCl_3$), and high resolution mass spectra (HRMS).[5] b) The number in the parentheses is a ratio of E- to Z-isomer estimated from that of peak height in the ^{31}P-NMR spectrum. c) E- and Z-isomers could be separated by thin-layer chromatography.

The present reaction may proceed as shown in Scheme 1.



3 **2** **1** **4**

a: X=O, R=H; b: X=O, R=Ph; c: X=S, R=H; d: X=S, R=Ph

Scheme 1.

That is, **1** undergoes phospha-Cope rearrangement to give a transient intermediate, "phospha-allene derivative" (**2**), which is trapped rapidly by alcohol to afford **3**. This is the first example for the phospha-Cope rearrangement of phospha-1-hexene-5-ynes. In competition with this rearrangement, Michael addition of alcohol to the triple bond of **1** occurs to give **4**. The substitution of phenyl group at 6-position makes the rearrangement as well as Michael addition slower, presumably because of its steric hindrance. Thus, the reaction of **1b,d** took a longer time than that of **1a,c**. It is noteworthy that in the reaction of the sulfides **1c,d** no Michael addition product was formed. It shows that activation energy of the rearrangement becomes relatively low in comparison with that of Michael addition in the case of the sulfide. A similar acceleration was also observed in the previous report.$^{1)}$

References

1) T. Kawashima, Y. Miki, T. Tomita, and N. Inamoto, Chem. Lett., 1986, 501.

2) See for example: D. K. Black and S. R. Landor, J. Chem. Soc., 1965, 6784.

3) E. Schaumann and F.-F. Grabley, Tetrahedron Lett., 1977, 4307; Justus Liebigs Ann. Chem., 1979, 1746.

4) E. Schaumann and F.-F. Grabley, Tetrahedron Lett., 21, 4251 (1980).

5) Physical and spectral data for **1b**, **3b**, and **4b** as typical examples: **1b**: Bp 180 °C/4x10^{-4} Torr. ^{31}P-NMR: δ_p 13.6 ppm. ^{1}H-NMR: δ 2.79 (dd, $^3J_{H,H}$=6.57 Hz, $^2J_{H,P}$=16.6 Hz, 2H, $C\underline{H}_2$), 4.62-4.97(m, 2H, $CH=C\underline{H}_2$), 5.17-5.61(m, 1H, $C\underline{H}=CH_2$), 6.79-7.11(m, 8H, C-Ph and m- and p-H of P-Ph), and 7.17-7.49(m, 2H, o-H of P-Ph). HRMS: m/z Found: 266.0873. Calcd for $C_{17}H_{15}OP$: 266.0861; **3b**: viscous oil. ^{31}P-NMR: δ_p 29.61 and 30.01 ppm (1:1). ^{1}H-NMR: δ 0.86(m, 3H, $-C\underline{H}_3$), 1.06-1.76(m, 8H, $OCH_2C_4\underline{H}_8$), 3.53-4.02(m, 4H, $OC\underline{H}_2-$ and $=CC\underline{H}_2CH=$), 4.80-5.29(m, 2H, $CH=C\underline{H}_2$), 5.32-6.00(m, 1H, $C\underline{H}=CH_2$), 6.13(d, $^2J_{H,P}$=17 Hz, 1H, $PC\underline{H}=C-$), 7.03-7.64(m, 8H, C-Ph and m- and p-H of P-Ph), and 7.64-8.11(m, 2H, o-H of P-Ph). HRMS: m/z Found: 368.1893. Calcd for $C_{23}H_{29}O_2P$: 368.1905; **4b**: viscous oil: ^{31}P-NMR: δ_p 39.24 and 39.63 ppm (1:1). ^{1}H-NMR: δ 0.87(m, 3H, $-C\underline{H}_3$), 1.26-1.70(m, 8H, $OCH_2C_4\underline{H}_8-$), 3.14(m, dd, $^3J_{H,H}$=7.96 Hz, $^2J_{H,P}$=14.5 HZ, 2H, $PC\underline{H}_2$), 3.42-3.94(m, 2H, $OC\underline{H}_2-$), 4.89-5.33(m, 2H, $-CH=C\underline{H}_2$), 5.49-6.51(m, 2H, $-C\underline{H}=CH_2$ and $PC\underline{H}=C-$), and 6.98-7.62(m, 10H, 2xPh). HRMS: m/z Found: 368.1925. Calcd for $C_{23}H_{29}O_2P$: 368.1905.

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