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THE PHOSPHA-COPE REARRANGEMENT OF 3-ARYL-3$^{\lambda}$-PHOSPHA-1,5-HEXADIENE DERIVATIVES

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The title compounds were refluxed in hexanol to give quantitatively the O-hexyl aryl-4-pentenylphosphinate derivatives via transient monomeric metaphosphinates, which seem to be formed by the phospha-Cope rearrangement. Kinetic studies show that the reaction rate increases with an increase in the magnitude of the positive charge on the phosphorus atom.

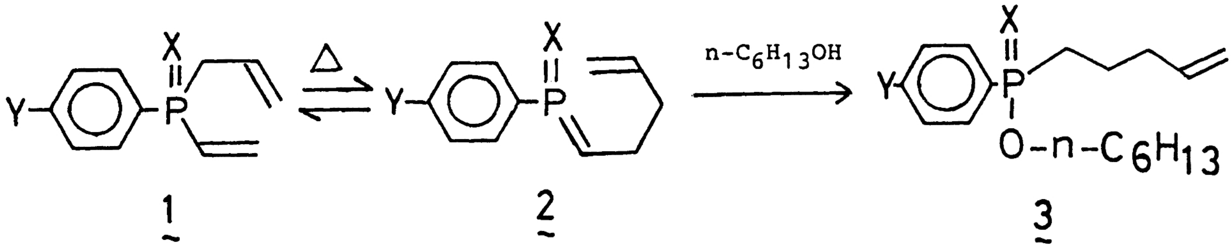
The Cope rearrangements involving hetero atoms have been an excellent method for the formation of carbon-hetero atom double bond. In particular, the Claisen rearrangement is an important synthetic method for the preparation of carbonyl compound and it has been often utilized as a key step for the synthesis of natural products.[1)]

There are many reports on the thio-Claisen rearrangements [2)] and cationic aza-Cope rearrangements,[3)] but a few reports on the phospha-Cope rearrangement.[4,5)] Loewus reported on the phospha-Cope rearrangement of sodium allylvinylphosphinate as a phosphorus analogue of oxide anion Cope rearrangement.[5)]

Here we wish to report a similar rearrangement of the title compounds and the substituent effects.

3-Phenyl-3$^{\lambda}$-phospha-1,5-hexadiene 3-oxide, 3-sulfide, and 3-selenide (**1a-c**)[6)] and 3-aryl-3$^{\lambda}$-phospha-1,5-hexadiene 3-sulfides (**1d-i**) were prepared as follows: Methyl allylphenylphosphinate was treated with thionyl chloride to give allylphenylphosphinyl chloride which was allowed to react with vinylmagnesium bromide at -78 °C in tetrahydrofuran to give **1a** in 74% overall yield. The sulfide (**1b**) and selenide (**1c**) were prepared by the reaction of **1a** with Lawesson's reagent, 2,4-

bis(p-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide, in toluene at 100 °C and by treatment of **1a** with phenylsilane in the presence of selenium in refluxing benzene in 65 and 72% yields, respectively. As described for **1b** the sulfides (**1d-i**) were prepared in ca. 40% yields from the corresponding ethyl allylarylphosphinates, which were given in 40-50% yields by subsequent reactions of diethyl allylphosphonate with thionyl chloride and arylmagnesium bromides.



a:X=O, Y=H; b:X=S, Y=H; c:X=Se, Y=H; d:X=S, Y=OMe; e:X=S, Y=Me; f:X=S, Y=SMe; g:X=S, Y=F; h:X=S, Y=Cl; i:X=S, Y=Br

Refluxing of 3-aryl-3λ-phospha-1,5-hexadiene derivatives (**1a-i**) (0.1 mmol) in hexanol (4 ml) for 48 h gave quantitatively the corresponding O-hexyl aryl-4-pentenylphosphinate derivatives (**3a-i**).[6)]

These products can be considered to be formed via transient monomeric metaphosphinates (**2**), which are produced by Cope rearrangement of **1**.[7)] Recently it has been reported that monomeric metaphosphinates can be synthesized as stable compounds from the corresponding methylenephosphines.[8)]

The reaction can be monitored by ^{31}P-NMR spectroscopy, indicating that the peak assignable to the product (**3**) increases with a decrease of that of the starting materials (**1**). Since the phosphine oxide (**1a**) is hygroscopic, it is necessary to be dried thoroughly before using, because of contamination with the product trapped by water.

The reaction rates were measured by means of gas chromatography, indicating that the reaction proceeds in pseudo first order with respect to **1** with the rate constants shown in Table 1. In Table 1, ^{31}P-NMR data of **1** and **3** are also shown.

It is very interesting to point out that the present reaction proceeds in much milder conditions than those described by Loewus [5)] in spite of the absence of the oxide anion group, that the rate constants increase in order of P=O, P=S, and P=Se (see the rate constants for **1a-c** in Table 1), and that the reaction is accelerated

Table 1. ^{31}P-NMR spectral data of **1a-i** and **3a-i** and rate constants

1	δ_P/ppm	**3** δ_P/ppm	k/s^{-1}	**1**	δ_P/ppm	**3** δ_P/ppm	k/s^{-1}
a:X=O, Y=H	26.5	44.5	1.0×10^{-5}	f:X=S, Y=SMe	35.9	92.6	1.9×10^{-5}
b:X=S, Y=H	36.4	92.7	1.9×10^{-5}	g:X=S, Y=F	35.7	91.6	2.2×10^{-5}
c:X=Se, Y=H	27.3	95.2	2.9×10^{-5}	h:X=S, Y=Br	36.0	91.1	2.2×10^{-5}
d:X=S, Y=OMe	35.7	92.5	1.7×10^{-5}	i:X=S, Y=Cl	35.9	91.7	2.5×10^{-5}
e:X=S, Y=Me	36.1	93.0	1.8×10^{-5}				

by the replacement of electron-withdrawing substituent at the para position of the phenyl group (see the rate constants for **1d-i** in Table 1).$^{9)}$ The last two results may be inconsistent each other judging from only electronegativities of O, S, and Se. However, considering a property of P=X bond in detail, it can be explained reasonably. It is well known that the double bond character of P=X bond decreases in order of P=O, P=S, and P=Se with an increase in the contribution of the canonical structure $\geqslant P^+{-}X^-$.$^{10)}$ An increase in the positive charge on a phosphorus atom is also brought about by substituent at the para position of the phenyl group, and it may play an important role to accelerate the reaction. In other words, in the transition state the positive charge induced on a phosphorus atom by these effects would make electron donation from allyl to vinyl moieties more favorable.

The present reaction provides a novel synthetic route to 4-pentenylphosphinates, possible precursors for synthesis of 1,5-hexadienes by application of the Horner-Emmons reaction.

Further investigations are in progress.

References

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2) For a recent review see: L. Morin, J. Leband, D. Paquer, R. Chanssin, and D. Barillier, Phosphorus and Sulfur, 7, 69 (1979).

3) For a recent review see: H. Heimgartner, H.-J. Hansen, and H. Schmid,"Iminium Salts in Organic Chemistry," ed by H. Böhme and H. G. Viehe, Wiley, New York (1979), Part 2, pp. 655-732.

4) For examples see: R. Appel, V. Barth, F. Knoll, and I. Ruppert, Angew. Chem., Int. Ed. Engl., 18, 873 (1979). R. Appel, J. Hünerbein, and F. Knoch, Angew.

Chem., Int. Ed. Engl., 22, 61 (1983), and references cited therein.

5) D. I. Loewus, J. Am. Chem. Soc., 103, 2292 (1981).

6) Physical and spectral data of **1a** and **3a** are shown as typical examples: **1a:** bp 140 °C/0.04 Torr: ^{1}H-NMR(CDCl$_3$): δ 2.88 (dd, $^3J_{H,H}$=7.1 Hz, $^2J_{H,P}$=15.5 Hz, 2H, P-C$\underline{H}_2$-CH=CH$_2$), 4.96-5.32 (m, 2H, P-CH$_2$-CH=C$\underline{H}_2$), 5.49-5.90 (m, 1H, P-CH$_2$-C$\underline{H}$=CH$_2$), 5.90-6.87 (m, 3H, P-C$\underline{H}$=C$\underline{H}_2$), 7.33-7.58 (m, 3H, aromatic meta and para), and 7.58-7.94 (m, 2H, aromatic ortho). ^{13}C-NMR(CDCl$_3$): δ_C 35.6 ppm (d, $^1J_{C,P}$=69.6 Hz, P-$\underline{C}$H$_2$-CH=CH$_2$), 119.7 (d, $^3J_{C,P}$=11.6 Hz, P-CH$_2$-CH=$\underline{C}$H$_2$), 126.1 (d, $^2J_{C,P}$=9.2 Hz, P-CH$_2$-$\underline{C}$H=CH$_2$), 127.7 (d, $^3J_{C,P}$=11.6 Hz, aromatic meta), 129.6 (d, $^2J_{C,P}$=9.2 Hz, aromatic ortho), 129.7 (d, $^1J_{C,P}$=93.4 Hz, P-$\underline{C}$H=CH$_2$), 130.9 (d, $^4J_{C,P}$=2.4 Hz, aromatic para), 131.0 (d, $^1P_{C,P}$=100.1 Hz, aromatic ipso), and 133.4 (s, P-CH=$\underline{C}$H$_2$). ^{31}P-NMR(CDCl$_3$): δ_P 26.5 ppm (from 85% H$_3$PO$_4$). IR(neat): $\nu_{P=O}$ 1230 cm^{-1}. Elemental analysis: Found: C, 68.47; H, 7.11%. Calcd for C$_{11}$H$_{13}$OP: C, 68.74; H, 6.82%. High resolution MS (70 eV): m/z Found: 192.0690. Calcd for C$_{11}$H$_{13}$OP: 192.0703.

3a: viscous oil: ^{1}H-NMR(CDCl$_3$): δ 0.72-1.03 (triplet like, 3H, O-(CH$_2$)$_5$-C$\underline{H}_3$), 1.03-2.27 (m, 14H, O-CH$_2$-(C$\underline{H}_2$)$_4$-, P-(C$\underline{H}_2$)$_3$-CH=CH$_2$), 3.54-4.23 (m, 2H, O-C$\underline{H}_2$-), 4.81-5.11 (m, 2H, -CH=C$\underline{H}_2$), 5.48-5.96 (m, 1H, -C$\underline{H}$=CH$_2$), 7.32-7.62 (m, 3H, aromatic meta and para), and 7.62-7.93 (m, 2H, aromatic ortho). ^{31}P-NMR(CDCl$_3$): δ_P 44.5 ppm. High resolution MS: m/z Found: 294.1722. Calcd for C$_{17}$H$_{27}$O$_2$P: 294.1747.

7) A possibility of [1,3]-rearrangement was ruled out by labeling experiments.

8) For examples see: R. Appel and C. Casser, Tetrahedron Lett., 25, 4109 (1984). R. Appel, F. Knoch, and H. Kunze, Angew. Chem., Int. Ed. Engl., 23, 157 (1984).

9) The following Hammet's equation was obtained for **1b** and **1d-i**: $\log k/k_0=+0.60\ \sigma_p$ (r=0.96, n=7).

10) T. A. Albright, W. J. Freeman, and E. E. Schweizer, J. Org. Chem., 40, 3437 (1975), and references cited therein. The contribution of the canonical structure can be estimated by the force constant. The force constants are calculated from frequencies of stretching vibration of P=X bond of **1a-c** to be 8.51x10^5, 4.81x10^5, and 3.34x10^5 (dyne cm^{-1}) for P=O, P=S, and P=Se bonds, respectively. It is surprising to point out that a linear relationship was observed between the rate constants and the force constants.

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