CHEMISTRY LETTERS, pp. 577-580, 1988.

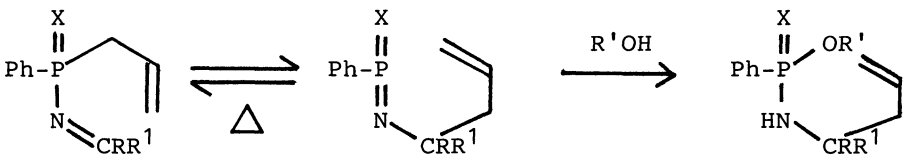
The Azaphospha-Cope Rearrangement of 2-Aza-3-phospha-1,5-hexadiene Derivatives

Takayuki KAWASHIMA,* Tsutomu KIHARA, and Naoki INAMOTO*

Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo 113

The 1-substituted title compounds can undergo the azaphospha-Cope rearrangement to give the corresponding (3-butenylimino)phosphine derivatives, which can be trapped by hexanol to afford the corresponding hexyl phenyl(3-butenylamido)phosphonates predominantly, whereas 1,1-disubstituted ones give the nucleophilic substitution products mainly. The activation parameters are presented for the reaction of 1-(4-nitrophenyl) derivative.

Appel and his coworkers have investigated on the phospha-Cope rearrangements of the hexadienes with more than two phosphorus atoms at various positions.[1] However, there is no report on the phospha-Cope rearrangement involving one more heteroatoms other than phosphorus atom till now, except for the example reported by Gareev and Pudovik.[2] Such circumstances and an expectation [3] that an introduction of an electron-attracting group to the position 1, 2, or 3 may cause to accelerate this rearrangement led us to investigate on 2-aza-3-phospha-1,5-hexadiene system, in which the carbon atom at 2-position is replaced by the more electronegative nitrogen atom. Here we wish to report on preliminary results of the title reaction.



1 2 3

1-Substituted 3-phenyl-2-aza-3-phospha-1,5-hexadiene derivatives (1)[4] were

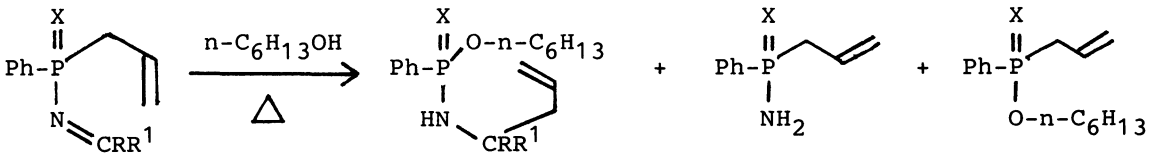
readily prepared by condensation reaction of the corresponding allylphenylphosphinic amide (**4**) with aldehydes in the presence of dehydrating reagent such as anhydrous magnesium sulfate in good conversion yields. 1,1-Diaryl derivatives were prepared from the corresponding phosphinyl chlorides and ketimides with triethylamine in moderate yields.

1-Substituted 3-phenyl-2-aza-3-phospha-1,5-hexadiene 3-sulfides (**1a-i**) (0.15-0.42 mmol) were refluxed in hexanol (2 ml) for 2-3 days to give mainly a mixture of diastereomers of hexyl phenyl(1-phenyl-3-butenylamido)thiophosphonates (**3a-i**)[5] with a small amount of allylphenylthiophosphinic amide (**4**)(a: X=S). Compound **3** seems to be a trapped product with an alcohol of the corresponding iminophosphine derivative, [6] which would be formed by the azaphospha-Cope rearrangement of **1** and **4** is presumed to be a solvolysis product at the C=N bond of **1**.

On the other hand, the reaction of 1,1-diaryl derivatives gave the corresponding hexyl allylphenylphosphinates (**5**), nucleophilic substitution (S_N2) products, besides the desired products. Use of secondary alcohols can retard the substitution reaction, but not so much. In the case of the reaction of **1j**, three types of reactions occurred. The results are summarized in Table 1.

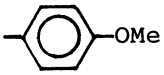
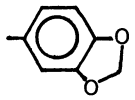
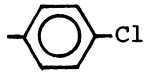
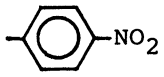
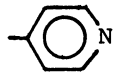
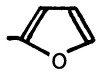
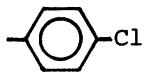
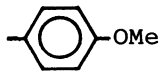
The sulfides gave the rearrangement products in higher yields than the oxides (see **1a** versus **1j** and **1k** versus **1n**). It is very interesting to point out that the S_N2 product was not obtained in most cases of 1-monosubstituted derivatives, while they were main products in the cases of 1,1-diaryl derivatives. It seems presumably to be due to retardation of the substitution reaction by the decrease in the ability of the imino group moiety to function as a leaving group and/or rate acceleration of the azaphospha-Cope rearrangement by steric effect at the bond-forming site. The percentage of the solvolysis at the C=N bond increases with the electron-donating property of the substituent group at 1-position, as observed in the hydrolysis of p- and m-substituted benzylidene-1,1-dimethylethylamines above pH 9.[7] Considering this electronic effect together with steric effect it can be reasonably explained that the reaction of 1,1-disubstituted derivatives gave no solvolysis products at the C=N bond in contrast to that of 1-substituted ones.

Finally, the kinetic study was carried out using **1f**, which gave no side reaction, and the present rearrangement was shown to occur with the following activation parameters, whose values are reasonable for the Cope rearrangement:[8] $\Delta H^{\neq}=94.1 \pm 4.2$ kJ mol^{-1} and $\Delta S^{\neq}=-95.3 \pm 10.5$ J mol^{-1} deg^{-1}.



1 3 4 5

Table 1. Thermal Reaction of **1** in Refluxing Hexanol[a)]

	1		Yields/%[b)]		
X	R	R^1	**3**[c)]	**4**	**5**
a: S	H	Ph	60	6	<1
b: S	H		64	11	-
c: S	H		54	15	-
d: S	H		71	11	-
e: S	H	-CH=CHPh	63	7	-
f: S	H		66	-	-
g: S	H		70	-	-
h: S	H		79	3	-
i: S	H	C_6F_5	77	-	-
j: O	H	Ph	40	20	40[d)]
k: O	Ph	Ph	50	-	50[d)]
l: O	Ph		20	-	80[d)]
m: O	Ph		-	-	100[d)]
n: S	Ph	Ph	86	-	14[d)]

a) All new compounds were fully characterized spectroscopically and by high resolution mass spectrometry. b) Isolated yields based on **1**. c) **3** was obtained as a diastereomer mixture in a ratio of 2:3 to 1:1 when $R \neq R^1$. The diastereomers could not be separated by column chromatography. d) Yields based on peak heights of the products in the ^{31}P-NMR spectrum.

References

1) 1,3,4,6-Tetraphospha-1,5-hexadiene: R. Appel, V. Barth, F. Knoll, and I. Ruppert, Angew. Chem., Int. Ed. Engl., 18, 873 (1979); 1,6-Diphospha-: R. Appel, V. Barth, B. Bruck, J. Hünerbein, F. Knoch, and W. Paulen, Nova Acta Leopoldine, 264, 39 (1985); 1,3-Diphospha-: R. Appel, J. Kochta, and F. Knoch, Chem. Ber., 120, 131 (1987); 3,4-Diphospha-: R. Appel, V. Winkhaus, and F. Knoch, Chem. Ber., 120, 125 (1987).

2) R. D. Gareev and A. N. Pudovik, Zh. Obshch. Khim., 45, 1897 (1975).

3) a) T. Kawashima, Y. Miki, T. Tomita, and N. Inamoto, Chem. Lett., 1986, 501; b) T. Kawashima, Y. Miki, and N. Inamoto, "Physical Organic Chemistry 1986, A Collection of the Invited Lectures Presented at the 8th IUPAC Conference on Physical Organic Chemistry, Tokyo, Japan, 24-29 August, 1986," ed by M. Kobayashi, Elsevier Science Publishers B. V., Amsterdam (1987), pp. 181-186.

4) **1a**: colorless viscous oil. IR (Neat): $\nu_{C=N}$ 1620 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 3.06 (dd, $^2J_{H,P}$=15.70 Hz, $^3J_{H,H}$=7.14 Hz, 2H, $PC\underline{H}_2$-), 4.79-5.38 (m, 2H, $CH=C\underline{H}_2$), 5.38-6.09 (m, 1H, $C\underline{H}=CH_2$), 7.13-7.71 (m, 6H, meta and para of 2XPh), 7.71-8.29 (m, 4H, ortho of 2XPh), and 9.21(d, $^3J_{H,P}$=39.3 Hz, 1H, $N=C\underline{H}Ph$). ^{13}C-NMR ($CDCl_3$): δ_C 41.67 (d,* $^1J_{C,P}$=69.0 Hz, P-$\underline{C}H_2$-), 120.1 (d, $^3J_{C,P}$=13.4 Hz, $-CH=\underline{C}H_2$), 127.0 (d, $^2J_{C,P}$=9.2 Hz, $-\underline{C}H=CH_2$), 127.7 (d, $^3J_{C,P}$=12.8 Hz, meta of P-Ph), 128.3 (s, meta of C-Ph), 129.7 (d, $^4J_{C,P}$=1.2 Hz, ortho of C-Ph), 130.9 (d, $^2J_{C,P}$=9.8 Hz, ortho of P-Ph), 131.2 (d, $^4J_{C,P}$=3.1 Hz, para of P-Ph), 132.4 (d, $^1J_{C,P}$=99.5 Hz, ipso of P-Ph), 133.0 (s, para of C-Ph), 134.6 (d, $^3J_{C,P}$=27.5 Hz, ipso of C-Ph), and 174.5 (d, $^2J_{C,P}$=7.9 Hz, $-N=\underline{C}H-$)(* This abbreviation shows the coupling pattern with phosphorus nucleus). ^{31}P-NMR ($CDCl_3$): δ_P 66.2. High resolution mass spectrum (HRMS) (70 eV): m/z Found: 285.0725. Calcd for $C_{16}H_{16}NPS$: 285.0740.

5) **3a**: colorless viscous oil as a diastereomeric mixture. IR(Neat): ν_{NH} 3280 cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 0.70-1.02 (m, 3H, $-C\underline{H}_3$), 1.02-1.46 (m, 6H, $-(C\underline{H}_2)_3CH_3$), 1.46-1.84 (m, 2H, $OCH_2C\underline{H}_2$-), 2.22-2.60 (m, 2H, $-C\underline{H}_2-CH=CH_2$), 3.24-3.65 (m, 1H, $N\underline{H}$), 3.65-4.60 (m, 3H, -CHPh and $OC\underline{H}_2$), 4.84-5.17 (m, 2H, $CH=C\underline{H}_2$), 5.17-5.87 (m, 1H, $C\underline{H}=CH_2$), 6.92-7.38 (m, 8H, $C-C_6\underline{H}_5$ and meta and para of P-Ph), and 7.38-8.00 (m, 2H, ortho of P-Ph). ^{31}P-NMR ($CDCl_3$): δ_P 74.2 and 73.8 (2:1). HRMS(70 eV): m/z Found: 387.1789. Calcd for $C_{22}H_{30}NOPS$: 387.1784.

6) The first electronically and sterically stabilized isolable iminophosphine sulfide (iminothioxophosphorane) was reported in the following paper: O. J. Scherer and N. Kuhn, Angew. Chem., Int. Ed. Engl., 13, 811 (1974). Most recently Markovski et al. have reported on the sterically protected stable oxo-, thioxo-, and selenoxo-imonophosphoranes: L. N. Markovski, V. D. Romanenko, and A. V. Ruban, Pure Appl. Chem., 59, 1047 (1987).

7) E. H. Cordes and W. P. Jencks, J. Am. Chem. Soc., 85, 2843 (1963).

8) 1,5-Hexadiene: W. v. E. Doering, V. G. Toscano, and G. H. Beasley, Tetrahedron, 27, 5299 (1971); 3-Oxa-1,5-hexadiene: C. J. Burrows and B. K. Carpenter, J. Am. Chem. Soc., 103, 6983 (1983); 3-Phospha-1,5-hexadiene 3-sulfide: Ref. 3b.

(Received December 5, 1987)