ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 595 (2000) 109–113

Journal of Organometallic Chemistry

Evidence for the involvement of pentacoordinate P-intermediates during the UV light-mediated fragmentation of a 2-phosphabicyclo[2.2.2]octene 2-oxide in the presence of O-nucleophiles

Stefan Jankowski [a,1], Juliusz Rudzinski [a], Helga Szelke [b], György Keglevich [b,*]

[a] *Department of Chemistry, Technical University of Lódź, 90-924 Lódź, Poland*
[b] *Department of Organic Chemical Technology, Technical University of Budapest, Muegyetem rkp. 3, H-1521 Budapest, Hungary*

Received 26 July 1999; received in revised form 20 August 1999; accepted 9 September 1999

Dedicated to Professor Emeritus Louis D. Quin (University of Massachusetts) by S. Jankowski and Gy. Keglevich for his outstanding achievements in P-heterocyclic chemistry.

Abstract

Isotope-exchange experiments with $H_2^{18}O$ proved at least the partial involvement of a P(V)-species (**8**) as an intermediate in the UV light-promoted fragmentation of phosphabicyclooctene (**1**). Selection between the alcohols of equimolar mixtures during the photochemical fragmentation of **1** also suggests a mechanism where an adduct (**4**) is formed in the rate-determining step affording the phosphorylated product (**5**) after decomposition. We were able to prove that the transient adduct (**4**) is formed in a reversible manner. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Photolysis; Fragmentation; Mechanism; Pentacoordinated intermediate; Reversibility; Nucleophility

1. Introduction

The UV light- or thermo-induced fragmentation of bridged heterocyclic systems, such as 2-phosphabicyclo[2.2.2]octa-5,7-diene 2-oxides [1–5] is a useful method for the generation of methylenephosphine oxides, a representative class of low-coordinate P-species that phosphorylate the nucleophiles added to the reaction mixture prior to the irradiation or to the heating.

Recently, it was substantiated by us that the UV light-mediated phosphorylation of alcohols by phosphabicyclo[2.2.2]octene 2-oxide **1** (used as the mixture of isomers **A** and **B**) may take place according to concurrent elimination–addition (EA) and addition–elimination (AE) mechanisms [6,7] (Scheme 1). The EA reaction path involves the formation of methylenephosphine oxide (**3**) in the rate-determining step followed by fast reaction with the alcohol or water present, while according to the AE mechanism, the nucleophile is added on the phosphoryl group of the phosphabicyclooctene (**1**) to form an intermediate with a pentacoordinate phosphorus atom (**4**), which is then fragmented to give the phosphorylated product (**5**).

In this paper we disclose further evidence for the involvement of pentacoordinate intermediate **4** and explore an interesting new detail on the mechanism of the fragmentation.

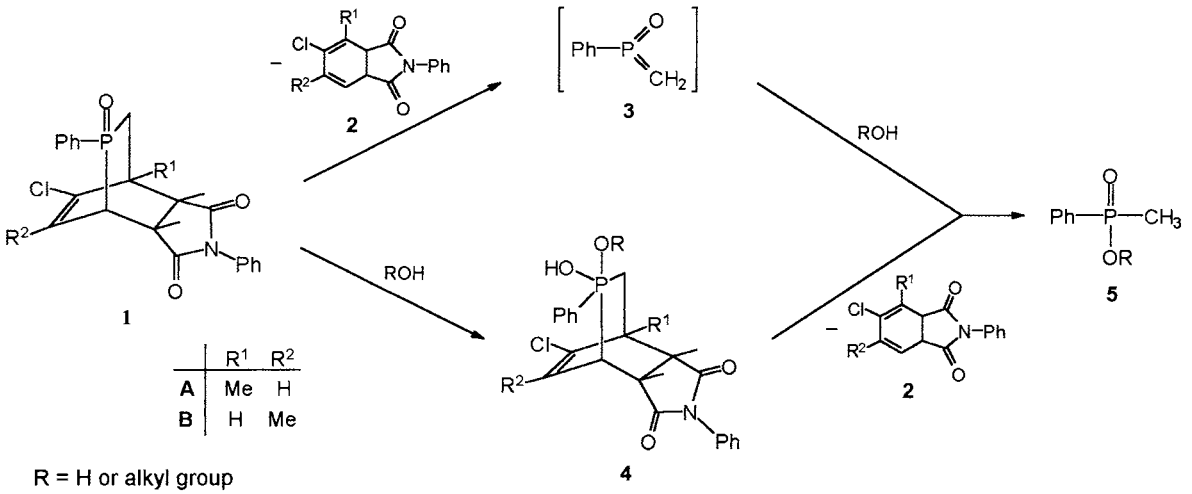
2. Results and discussion

2.1. Photolysis of phosphabicyclooctene (1) in the presence of $H_2^{18}O$

The overall quantum yield for the fragmentation of phosphabicyclooctene (**1**) is 0.040 ± 0.004 and is significantly lower than the yield for the photolysis of 2,3-oxaphosphabicyclo[2.2.2]octene derivatives, which are precursors of metaphosphates YPO_2 ($Y = EtO$, Et_2N;

* Corresponding author. Tel.: +36-1-4631111/5853; fax: +36-1-4633648.
E-mail address: keglevich@oct.bme.hu (G. Keglevich)
[1] Also corresponding author.

PII: S0022-328X(99)00588-4



Scheme 1.

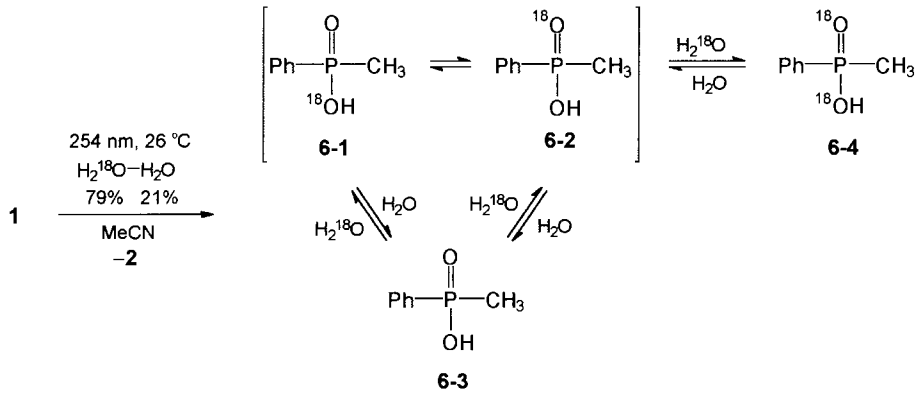
the average quantum yield is nearly 0.3) [8]. The difference in photostability is not the only discrepancy between these two systems. While the rate of the photolytic fragmentation of 2,3-oxaphosphabicyclo[2.2.2]octenes was found to be independent of the presence and concentration of alcohols [8], the rate of the photolysis of phosphabicyclooctene (**1**) depended on the concentration of alcohols [6,7] suggesting the possibility of the AE mechanism. To get an unequivocal proof of presence or absence of the pentacoordinate adduct (**4**) (Scheme 1), we decided to perform the photolysis in the presence of $H_2^{18}O$. Phosphinic acid (**6**) should contain ^{18}O independently of the mechanism of the reaction, but the starting P-heterocycle (**1**) should be labeled with ^{18}O only if intermediate **4** is involved and if the formation of intermediate **4** is reversible.

The mixture of acids **6**–**1** ⇆ **6**–**2**, **6**–**3** and **6**–**4** obtained after 120 min of irradiation (Scheme 2) was converted into the corresponding methyl esters **7**–**1**, **7**–**2**, **7**–**3** and **7**–**4**, respectively (Scheme 3) to improve the resolution of ^{31}P-NMR spectra. The products (**7**–**1**, **7**–**2**, **7**–**3** and **7**–**4**) could be identified by the four resonances at 45.397 (30%), 45.379 (32%), 45.427 (22%) and 45.351 (16%) that were due to the ^{18}O-induced perturbation. The upfield shift induced by ^{18}O is within the range observed before for single and double P–O bonds [9]. From relative signal intensities, the ^{18}O enrichment of PhP(O)(OMe)(Me) was estimated to be approximately 47%. The theoretical value from enriched water (79.3%) was 39.6%. The higher experimental value could be from an isotope exchange to result in the formation of **6**–**4** (Scheme 2).

For the signal of phosphabicyclooctene (**1**), no splitting by ^{18}O was observed in the ^{31}P-NMR spectra, so we decided to apply the more sensitive technique of FAB mass spectrometry. The starting material (**1**) isolated by chromatography from the reaction mixture was analyzed by FAB-MS and we experienced a significant isotope exchange comparing the ^{18}O:^{16}O ratios obtained with increasing reaction time (Table 1). The increase by 1.2% for phosphabicyclooctene (**1**) after 120 min of irradiation (simultaneously fragmentation occurs in 70%) corresponds to 0.3% of theoretically possible exchange. For the sample that was not irradiated and recovered immediately, or kept in darkness for 240 min, the pairs of isotopic ratios are the same and correspond to the natural abundance. This means that the isotopic exchange occurs only on irradiation. We attribute the incorporation of ^{18}O into phosphabicyclooctene (**1**) to the formation of pentacoordinate intermediate **8** (Scheme 4). The relatively small incorporation of ^{18}O in **1** may originate from three factors: the AE mechanism is less competitive than the EA mechanism, the equilibrium between **1** and **4** is shifted towards **4** and the decomposition of adduct **4** is much faster than its return to starting compound **1** (Scheme 5). A more significant equilibrium enrichment of ^{18}O in **1** could be reached only if the isotope exchange is much faster then fragmentation. Anyway, we could find evidence for the involvement of pentacoordinated intermediate **4** during the photolysis of **1** in the presence of water, as reversibility is possible only in this case.

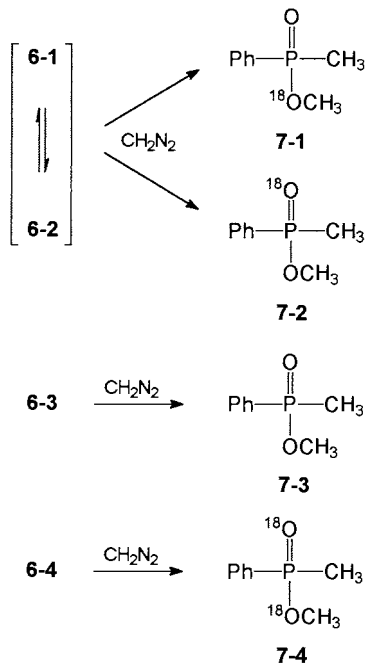
2.2. Photolysis of phosphabicyclooctene (1) in the presence of equimolar mixtures of alcohols

Our idea was that the phosphabicyclooctene (**1**) should select between the alcohols if the AE mechanism is effective; with the EA mechanism operating, there should not be a significant discrimination, as the highly reactive methylenephosphine oxide (**3**) [10] should not differentiate between the alcohol to a large extent. The photolysis of **1** was performed in an equimolar mixture



Scheme 2.

of methanol–ethanol, methanol–1-propanol and ethanol–2,2,2-trifluoroethanol. As we expected, there was a significant selection between the alcohols (Scheme 6). Methanol was more reactive than ethanol or 1-propanol, as PhMeP(O)OMe predominated over PhMeP(O)OEt or PhMeP(O)OnPr in the reaction mixtures (58 vs. 42% and 63 vs. 37%, respectively). Ethanol proved to be more than twice as efficient as compared with 2,2,2-trifluoroethanol: 71% of PhMeP(O)OEt and 29% $PhMeP(O)OCH_2CF_3$ were detected in the reaction mixture. The above observations show clearly the role of nucleophility in the fragmentation, suggesting at least the partial involvement of the AE mechanism (Scheme 1). Due to its smaller pK_a, methanol is more reactive than ethanol or 1-propanol (15.09 vs. 15.93 and 16.1, respectively) [11]. 2,2,2-Trifluoroethanol is acidic (pK_a = 12.39), but is the least nucleophilic in the above series of alcohols.



Scheme 3.

3. Experimental

3.1. General

^{31}P-NMR spectra were recorded on an Bruker Avance DPX 250 spectrometer at 101.25 MHz, or on a Bruker DRX-500 instrument at 202.4 MHz. Water with 79.3% enrichment of ^{18}O was supplied by Techsnabeksport (USSR).

3.2. Photochemical fragmentation of phosphabicyclooctene (1) in the presence of $H_2^{18}O$

A solution of **1** and $H_2^{18}O$ in acetonitrile (10 ml) freshly distilled over P_2O_5 in a quartz tube was placed in the center of a Rayonet photochemical reactor fitted with eight low-pressure mercury lamps (253.7

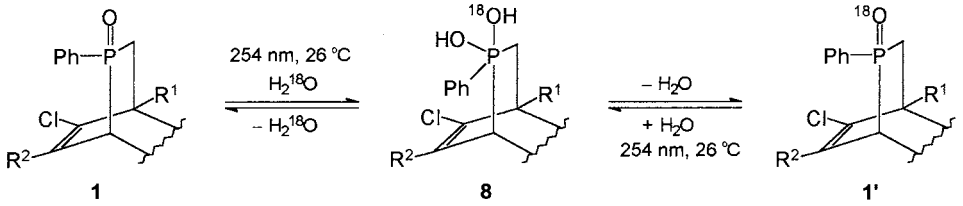
Table 1
Photochemical isotope exchange between **1** and $H_2^{18}O$ [a]

Time of irradiation (min)	Isotopic ratios in **1** after irradiation [b]	
	I_{414}/I_{412}	I_{416}/I_{412}
0	0.3857 ± 0.0014	0.0181 ± 0.0004
40	0.3901 ± 0.0015	0.0231 ± 0.0006
80	0.3933 ± 0.0019	0.0277 ± 0.0010
120	0.3973 ± 0.0017	0.0300 ± 0.0010
240 [c]	0.3847 ± 0.0020	0.0187 ± 0.0012

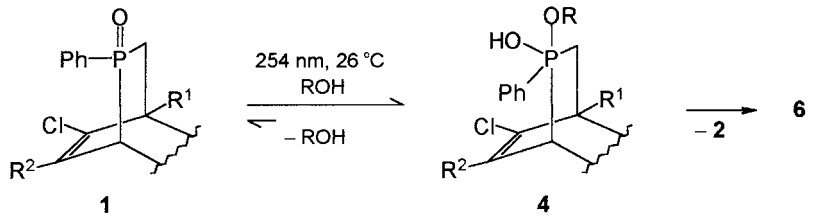
[a] The photolysis was carried out in the presence of 110 equivalents of $H_2^{18}O$; the initial concentration of **1** was 6.5 mmol l^{-1}.

[b] 412, M+H (^{35}Cl, ^{16}O); 414, M+H+2 (^{37}Cl, ^{16}O or ^{35}Cl, ^{18}O); 416, M+H+4 (^{37}Cl, ^{18}O).

[c] Without irradiation.



Scheme 4.



Scheme 5.

nm). The solution was irradiated with a light intensity of 14×10^{-7} Einstein (min ml)$^{-1}$. The solution was flushed with dry argon during irradiation. Temperature was constant at 25°C. The irradiation was stopped when about 70% of substrate was consumed, the solution was then evaporated to dryness in vacuo and an ethereal solution of excess of diazomethane was added to convert acid **6** into methyl ester **7**. The solution was again evaporated to dryness and examined by ^{31}P-NMR. Substrate **1** was isolated by chromatography on a silica gel plate (Merck, layer thickness 2 mm) using 5% MeOH in chloroform as the eluant ($R_f = 0.15$) followed by crystallization from ethyl acetate–*n*-pentane.

Samples obtained in the above way were subjected to mass spectrometric analysis. The isotopic ratios were measured using a hybrid FAB-isotope ratio spectrometer MI 1201 E (PO Elektron, Ukraine). Samples of about 0.3 mg were dissolved in about 5 μl of 3-nitrobenzyl alcohol. A total of 1–2 μl of the solution was placed on the copper tip of the direct insertion probe. The mean values of $[M^+ + 3]/[M^+ + 1]$ or $[M^+ + 5]/[M^+ + 1]$ (protonated positive ions) isotopic ratios were obtained from up to 30 separate determinations, each being an average of ten individual measurements.

3.3. Determination of the quantum yield

A solution of starting material **1** (0.0097 mol l^{-1}) and water (1.37 mol l^{-1}) in acetonitrile (30% of CD_3CN) was irradiated up to 120 min. Photolysis was interrupted at time intervals of 20 min and 1 ml of solution was taken for ^{31}P-NMR analysis. To determine the change of concentration of the substrate (**1**), ^{31}P-NMR peak areas were compared to a 2% solution of H_3PO_4 in water in an internal sealed capillary coaxially placed in an NMR tube. Spectra were run with 90° pulse and 10 s intervals. The quantum yield of fragmentation of compound **1** was found to be equal to 0.040 ± 0.004.

3.4. Photochemical fragmentation of phosphabicyclooctene (*1*) in equimolar mixtures of alcohol pairs

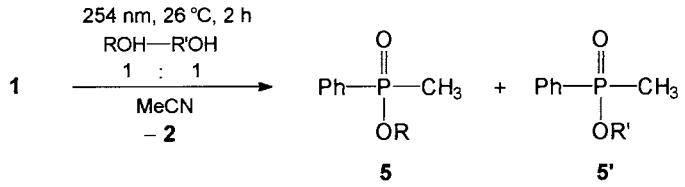
The mixture of 0.1 g (0.243 mmol) of phosphabicyclooctene (**1**) consisting of 61% of the **A** isomer and 39% of the **B** isomer, 0.049 mol of ROH and 0.049 mol of R′OH (Scheme 6) in 45 ml of acetonitrile was irradiated in a photochemical reactor with a mercury lamp (125 W) for 1.5 h. Volatile components were removed and the residue so obtained purified by flash column chromatography (silica gel, 3% methanol in chloroform) to give a mixture of the corresponding phosphinates (**5** and **5′**) as shown in Scheme 6.

Entry 1: 2.0 ml of methanol and 2.9 ml of ethanol; yield of **5** and **5′**: 87%.

Entry 2: 2.0 ml of methanol and 3.7 ml of 1-propanol; yield of **5** and **5′**: 84%.

Entry 3: 2.9 ml of ethanol and 3.6 ml of 2,2,2-trifluoroethanol; yield of **5** and **5′**: 79%.

5′ (R′ = CF_3CH_2): GC–MS, *m*/*z* (relative intensity) 238 (M^+, 45), 237 (61), 223 (M–Me, 24), 219 (M–F, 10), 218 (13), 140 (100), 139 (M–CF_3CH_2O, 41), 125 (PhPO, 49), 77 (Ph, 85).



R	R'	[%][a]		entry
Me	Et	58 (δ_P 44.9)[b]	42 (δ_P 43.0)[c]	(1)
Me	n-Pr	63 (δ_P 44.8)[b]	37 (δ_P 42.8)[d]	(2)
Et	CF_3CH_2	71 (δ_P 42.8)[c]	29 (δ_P 49.4)	(3)

[a] based on relative ^{31}P NMR intensities; [b] δ_P [6] 44.8; [c] δ_P [6] 42.7; [d] δ_P [6] 42.8

Scheme 6.

Acknowledgements

This work was partially supported by the Technical University of Lódź (S.J. and J.R.). Gy.K. thanks the Ministry of Higher Education for financing this project (Grant no. FKFP 363/1999). The OTKA support is also acknowledged (Grant no. T 029039).

References

[1] L.D. Quin, J.-S. Tang, Gy. Keglevich, Heteroat. Chem. 2 (1991) 283.
[2] L.D. Quin, J.-S. Tang, G.S. Quin, Gy. Keglevich, Heteroat. Chem. 4 (1993) 189.
[3] Gy. Keglevich, K. Újszászy, L.D. Quin, G.S. Quin, Heteroat. Chem. 4 (1993) 559.
[4] Gy. Keglevich, L. Tõke, Zs. Böcskei, D. Menyhárd, L.D. Quin, Heteroat. Chem. 6 (1995) 593.
[5] Gy. Keglevich, K. Újszászy, G.S. Quin, L.D. Quin, Phosphorus Sulfur 106 (1995) 155.
[6] Gy. Keglevich, K. Steinhauser, K. Ludányi, L. Tõke, J. Organomet. Chem. 570 (1998) 49.
[7] Gy. Keglevich, K. Steinhauser, Gy. M. Keserû, Zs. Böcskei, K. Újszászy, Gy. Marosi, I. Ravadits, L. Tõke, J. Organomet. Chem. 579 (1999) 182.
[8] S. Jankowski, L.D. Quin, J. Am. Chem. Soc. 113 (1991) 7011.
[9] C. Roeske, P. Paneth, M.H. O'Leary, W. Reimschüssel, J. Am. Chem. Soc. 107 (1985) 1409.
[10] H. Heydt, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme Verlag, Stuttgart, 1990, p. 381 (Chapter E/2.2).
[11] J.F. Stoddart, in: D. Barton, W.D. Ollis (Eds.), Comprehensive Organic Chemistry, vol. 1, Pergamon, Oxford, 1979, p. 584.