Heteroatom Chemistry
Volume 8, Number 2, 1997

Photolysis of 7-(2,4,6-Trialkylphenyl-)7-Phosphanorbornene 7-Oxides in the Presence of Protic Species

György Keglevich*

Department of Organic Chemical Technology, Technical University of Budapest, 1521 Budapest, Hungary

Krisztina Ludányi

Central Research Institute of Chemistry for Hungarian Academy of Sciences, 1525 Budapest, Hungary

Louis D. Quin

Department of Chemistry, University of Massachusetts, Amherst, MA 01003

Received 11 July 1996; revised 16 September 1996

ABSTRACT

Irradiation of 7-(2,4,6-trialkylphenyl-)7-phosphanorbornene 7-oxides at 254 nm in the presence of alcohols or water led to H-phosphinic acid derivatives. The experimental data are consistent with the mechanism established earlier for P-phenyl derivatives, involving a five-coordinate adduct from the interaction of the phosphanorbornene and the protic species which then fragments. There is no evidence that the larger substituent allowed a competing reaction to occur where the first step is unimolecular fragmentation to a two-coordinate phosphoryl species. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

It is well-known that the photolysis of 7-phosphanorbornene 7-oxides in alcohols leads to H-phosphinates [1–3]. Earlier, the fragmentations were believed to proceed through free two-coordinate intermediates (Y–P=O; Y=Ph, ArO) [1,2]. Quin et al. have proven recently that five-coordinate species formed by the attack of alcohol on the P atom of the phosphanorbornene are the real intermediates of the reactions [3].

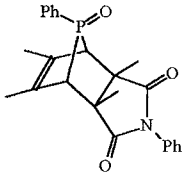
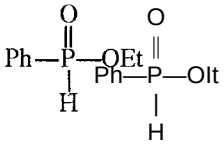
In this article, the fragmentations and related phosphorylations are extended to phosphanorbornenes with sterically demanding P substituents. With such substituents, it was considered possible that the addition of the alcohol to form a five-coordinate intermediate might be repressed, thus allowing an opportunity for the unimolecular fragmentation to a two-coordinate phosphoryl species to occur.

RESULTS AND DISCUSSION

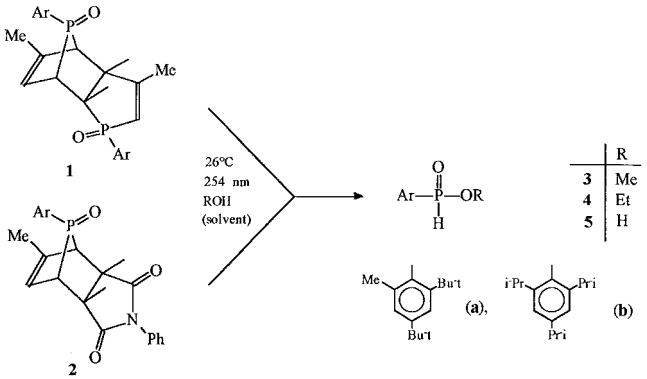
The phosphole oxide dimers (**1a,b**) and the Diels-Alder cycloadducts (**2a,b**) were available from our earlier work [4,5]. Photolyses of **1** and **2** were carried out at 254 nm at room temperature in the presence of solvents [CH_3CN, $(CH_2Cl)_2$, or excess of methanol or ethanol] in 5 mm NMR tubes. Depending on the

To whom correspondence should be addressed.

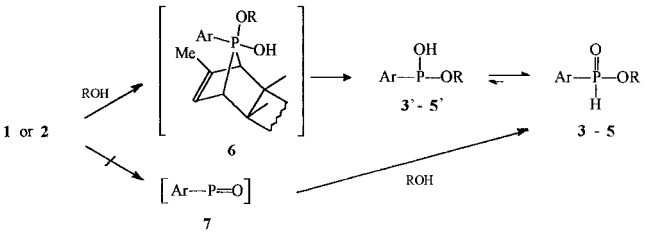
1042-7163/97/020135-03

entry	starting material	ROH	solvent	reaction time	product	yield	^{31}P NMR	erature[a]
1.)	**1a**	MeOH	CH_3CN	18h	**3a**	69%	32.9	
2.)	**1b**	MeOH	CH_3CN	20h	**3b**		26.8	NMR
3.)	**1a**	EtOH	CH_3CN	18h	**4a**	70%	30.1	
4.)	**2a**	MeOH	CH_3CN	8h	**3a**		31.2	2.9 3.8
5.)	**1b**	H_2O	CH_3CN	b	**5b**	65%	22.8	0.1 1.2
6.)	**1b**	MeOH		14h	**3b**	72%	26.9	2.8 3.9
7.)	**1b**	EtOH		9h	**4b**	70%	23.6	3.6
8.)	**2b**	EtOH	$(CH_2Cl)_2$	30h	**4b**		+3.6	3.6
9.)		EtOH	$(CH_2Cl)_2$	7h			24.4[c] lit.[3]: 26.8	24.4[c] Ref. [3]: 26.8

[a]See Experimental for general procedure.
[b]Not determined
[c]^1J(P,H) = 562.1 Hz, Ref. [3]: 568.0.



SCHEME 1



SCHEME 2

protic reactant (methanol, ethanol, or water), H-phosphinic acid derivatives **3–5** were the products (Scheme 1). The reactions were monitored by ^{31}P NMR spectroscopy. Experimental details are given in Table 1. After flash column chromatography, the phosphinic species (**3a,b**, **4a,b**, and **5b**) were obtained in 65–72% yield and with a purity of 90–95%. The products (**3–5**) were identified by ^{31}P and ^{1}H NMR and mass spectral data. The P(O)H moiety in **3–5** was easily recognized from the characteristic ^1J(P,H) couplings of 549–557 Hz. The molecular ions were confirmed by HRMS peak match.

Regarding the photolyses, our observations can be summarized as follows. All fragmentations took place cleanly, practically without side reactions. Depending on the reactants and the solvent, completion of the reactions required 8–30 hours. It was found that Diels-Alder cycloadduct **2a** underwent faster fragmentation than dimer **1a** (entries 4 and 1) and that the fragmentation was much slower in 1,2-dichloroethane than in acetonitrile (entries 8 and 4). Critical observations were that the rate of the fragmentation of the trialkylphenyl-phosphanorbornenes (e.g., **1b**) depended on the concentration of the alcohol (entries 2 and 6) and that the tri-isopropylphenyl-phosphanorbornene (**2b**) was fragmented much slower than the P-phenyl derivative (entries 8 and 9). Dependency of the rate of fragmentation on the alcohol concentration observed with **1b** suggests that the rate-determining step involves a bimolecular attack. This is also confirmed by the steric hindrance caused by the *ortho* alkyl substituent of **2b**. These observations are consistent with the mechanism proposed earlier [3] involving a five-coordinate species (**6**) formed by the attack of the alcohol on the P atom of the phosphanorbornene in the first (rate-determining) step. This is then followed by the fast decomposition of each intermediate **6** to the respec-

tive trivalent P species **3′–5′** that is in tautomeric equilibrium with products **3–5** (Scheme 2). Accordingly, occurrence of the fragmentation through two-coordinate species **7** can be rejected, and therefore it can be concluded that the large P substituent has had no influence on the outcome of the reaction.

We wished to evaluate also the effect of the sterically demanding P substituent on the thermal stability of the phosphole oxide dimer. For this purpose, phosphanorbornene **1b** was subjected to thermal examinations. TG, DTG, and DSC examinations showed that dimer **1b** and the P-phenyl derivative [**1**, Ar = Ph (**c**)] had more or less the same thermostability; **1b** and **1c** underwent ejection of the P moiety in the range of 235–270°C and 220–255°C, respectively. Both fragmentations are exothermic.

EXPERIMENTAL

FT ^{31}P NMR spectra were recorded with an IBM NR-80 spectrometer using 85% H_3PO_4 as external standard with internal lock. Downfield shifts have positive signs. ^{1}H NMR spectra were recorded with a Bruker DRX-500 spectrometer with Me_4Si as an internal standard. Coupling constants are given in hertz. The mass spectra were obtained on an MS-902 instrument at 70 eV.

Photolyses were conducted in an Ace Glass quartz, water-cooled immersion well with a 450W Hanovia medium-pressure lamp (nominally 254 nm).

The phosphanorbornenes (**1a,b** and **2a,b**) were prepared as described earlier [4,5].

General Procedure for the Preparation of Phosphinic Derivatives (**3a,b, 4a,b**, *and* **5b**)

A mixture of 0.095 mmol of the phosphanorbornene (**1a,b**, **2a,b**) and 0.15 mL of the protic species (methanol, ethanol, or water) in 0.5 mL of solvent [CH_3CN, $(CH_2Cl)_2$, or excess alcohol] was placed in a 5 mm EPR precision quartz tube that was then attached to the outer wall of the Ace immersion well. The irradiation at 254 nm was continued until the starting material had disappeared. Solvent was then evaporated and the crude product so obtained purified by flash column chromatography (silica gel, 3% methanol in chloroform) to give **3a,b**, **4a,b**, and **5b** with a purity of 90–95% according to the data summarized in Table 1.

The following products were thus prepared:

Methyl 2,4-di-tert-butyl-6-methylphenyl-H-phosphinate (**3a**) was prepared according to entry 1 of Table 1; ^{31}P NMR ($CDCl_3$) δ 32.9, ^1J(P,H) = 552.5, ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 9H, ortho-C(CH_3)$_3$, 1.54 (s, 9H, para-C(CH_3)$_3$, 2.75 (s, 3H, 6-CH_3), 3.89 (d, ^3J(P,H) = 12.2, 3H, OCH_3), 8.40 (d, ^1J(P,H) = 562.2, 1H, P(O)*H*); MS, *m/z* (rel. int.) 282 (M^+, 100), 267 (M–Me, 25), 189 (267$^-$HP(O)OMe$^+$H, 9), 57 (Bu, 90); HRMS, M^+_{found} = 282.1811, $C_{16}H_{27}O_2P$ requires 282.1749.

Methyl 2,4,6-tri-isopropylphenyl-H-phosphinate (**3b**) was prepared according to entry 6 of Table 1; ^{31}P NMR ($CDCl_3$) δ 26.9, ^1J(P,H) = 551.0; ^{1}H NMR ($CDCl_3$) δ 1.24 (d, ^3J(H,H) = 6.6, 12H, ortho-CH(CH_3)$_2$), 1.29 (d, ^3J(H,H) = 6.8, 6H, para-CH(CH_3)$_2$), 3.84 (d, ^3J(P,H) = 12.5, 3H, OCH_3), 8.02 (d, ^1J(P,H) = 551.2, 1H, P(O)*H*); MS, *m/z* (rel. int.) 282 (M^+, 100), 267 (M–Me, 80), 253 (267$^-$Me$^+$ H, 30), 239 (M–Pr, 25), 189 (267$^-$HP(O)OMe$^+$H, 42), 43 (Pr, 38); HRMS, M^+_{found} = 282.1808, $C_{16}H_{27}O_2P$ requires 282.1749.

Ethyl 2,4-di-tert-butyl-6-methylphenyl-H-phosphinate (**4a**) was prepared according to entry 3 of Table 1; ^{31}P NMR ($CDCl_3$) δ 30.1, ^1J (P,H) = 550.0; MS, *m/z* (rel. int.) 296 (M^+, 15), 281 (M–Me, 18), 253 (281$^-$Et$^+$H, 17), 189 (281$^-$HP(O)OEt$^+$ H, 29), 57 (Bu, 100); HRMS, M^+_{found} = 296.1963, $C_{17}H_{29}O_2P$ requires 296.1905.

Ethyl 2,4,6-tri-isopropylphenyl-H-phosphinate (**4b**) was prepared according to entry 7 of Table 1; ^{31}P NMR ($CDCl_3$) δ 23.6, ^1J(P,H) = 549.1; MS, *m/z* (rel. int.) 296 (M^+, 100), 281 (M–Me, 16), 253 (281$^-$Et$^+$H, 23), 189 (281$^-$HP(O)OEt$^+$H, 23), 43 (Pr, 22); HRMS, M^+_{found} = 296.1968, $C_{17}H_{29}O_2P$ requires 296.1905.

2,4,6-tri-isopropylphenyl-H-phosphinic acid (**5b**) was prepared according to entry 5 of Table 1; ^{31}P NMR ($CDCl_3$) δ 22.8, ^1J(P,H) = 556.7; MS, *m/z* (rel. int.) 268 (M^+, 100), 253 (M$^-$Me, 57), 189 (253$^-$HP(O)OH$^+$H, 22), 43 (Pr, 28); HRMS, M^+_{found} = 268.1643, $C_{15}H_{25}O_2P$ requires 268.1592.

ACKNOWLEDGMENT

Gy. Keglevich thanks the OTKA support of this work (Grant Numbers T 014917 and U 21513).

REFERENCES

[1] H. Tomioka, Y. Hirano, Y. Izawa, *Tetrahedron Lett.*, 1974, 4477.
[2] H. Tomioka, S. Miura, Y. Izawa, *Tetrahedron Lett., 24,* 1983, 3353.
[3] L. D. Quin, S. Jankowski, J. Rudzinski, A. G. Sommese, X.-P. Wu, *J. Org. Chem., 58,* 1993, 6212.
[4] L. D. Quin, Gy. Keglevich, A. Ionkin, R. Kalgutgar, G. Szalontai, *J. Org. Chem.,* 1996, in press.
[5] Gy. Keglevich, L. D. Quin, Zs. Böcskei, Gy. M. Keserũ, R. Kalgutkar, P. Lahti, *J. Organomet. Chem.,* 1996, in press.