Heteroatom Chemistry
Volume 12, Number 1, 2001

Study on the UV Light-Mediated Fragmentation of 7-(2,4,6-trialkylphenyl-)7-Phosphanorbornene 7-Oxides in Alcohols: New Evidences on the Mechanism

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Received 13 June 2000; revised 21 July 2000

ABSTRACT: *Preparative-scale photolyses of the title triisopropylphenyl-substituted compounds* **1** *and* **4** *at 254 nm, in the presence of alcohols, led to aryl-H-phosphinates* **3** *in good yields. Reaction of the tri-tert-butylphenyl derivative* **5** *was, however, accompanied by side reactions. The results of two series of competitive reactions are consistent with a mechanism involving a five-coordinate adduct* **8** *of the alcohol on the P=O group of the phosphanorbornene oxides.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:6–9, 2001

INTRODUCTION

The photolysis of 7-phosphanorbornene 7-oxides in alcohols is known to afford H-phosphinates YP(O)(OR)H, Y = Ph, Ar, and ArO [1–4]. This method is a good preparation of H-phosphinates, and its mechanism is also of interest. While earlier a fragmentation was assumed involving the two-coordinate intermediate Y–P=O [1,2], Quin et al. have recently pointed out the intermediacy of pentacoordinate species formed by the attack of alcohol on the P=O group of the phosphanorbornene [3]. Later on, the use of phosphanorbornenes with sterically demanding P-substituents in the above photolyses has led to a similar conclusion [4].

In this article, we disclose new results on the UV light-mediated fragmentation of P-aryl phosphanorbornenes in the presence of alcohols. A preparative-scale procedure is described for the synthesis of aryl-H-phosphinates, and new evidence is shown to support the involvement of a pentacoordinate intermediate during the photolyses.

RESULTS AND DISCUSSION

The earlier photolyses of trialkylphenyl-phosphanorbornenes involved 5 mm quartz NMR tube experiments [4]. We have now found that ca. 0.2 g quantities of phosphole oxide dimer **1** or the oxidized phosphole *N*-phenylmaleimide cycloadduct **4**, both with a 2,4,6-triisopropylphenyl substituent on the phosphorus atom, were efficiently photolysed in acetonitrile solution, in the presence of an alcohol,

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Contract Grant Sponsor: Ministry of Higher Education.
Contract Grant Number: 363/1999.
Contract Grant Sponsor: Hungarian Scientific Research Fund.
Contract Grant Number: T 029039.
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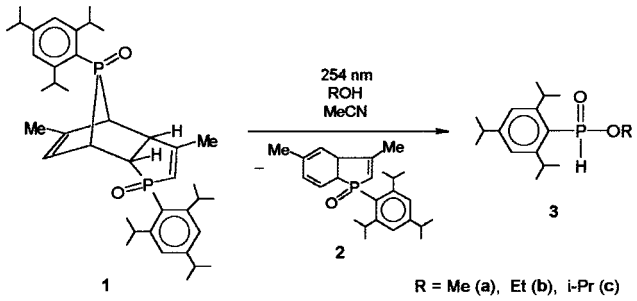
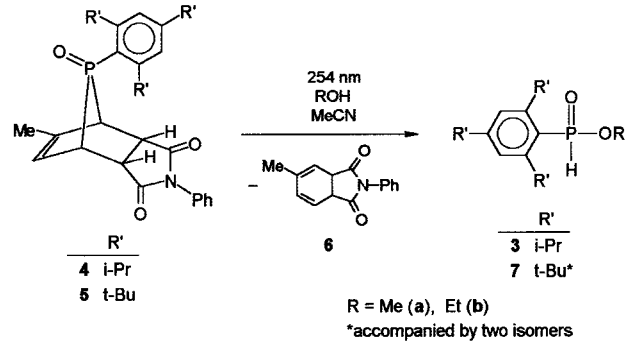
using a quartz photochemical reactor with a 125 W mercury lamp to give the aryl-H-phosphinates **3a–c** in quantitative conversions after a 3.5–4 hour irradiation (Schemes 1 and 2, entries 1–5 of Table 1). It was found, however, that the photolysis of the phosphanorbornene **5** with a 2,4,6-tri-*tert*-butylphenyl group on the phosphorus atom in the presence of methyl alcohol resulted in a mixture of three major isomers of the H-phosphinate (**7a**, **7a′**, and **7a″**); according to GC-MS, all three species were of a molecular weight of $m/z = 324$ (Scheme 2, entry 6 of Table 1).

Purification by column chromatography furnished the H-phosphinates (**3a–c** and **7a**, the latter being accompanied by isomers **7a′** and **7a″**) in 82–96% yield that were identified by ^{31}P NMR chemical shifts and significant $^{1}J_{PH}$ couplings (Table 1). Elemental composition of the new products (**3c, 7a, 7a′,** and **7a″**) was confirmed by HR-MS. The three isomers **7a**, **7a′**, and **7a″** obtained from the photolysis of precursor **5** in the presence of methanol displayed distinct mass spectra (Table 2). Due to the close resemblance to the spectrum of the 2,4,6-triisopropylphenyl derivative **3a**, the component formed in 37% yield was assumed to be the expected product **7a.** At this stage of the work, the structures of the other two isomers are uncertain, but the isomerization seems to be connected with the *tert*-butyl group.



SCHEME 1



SCHEME 2

Gas chromatography–mass spectrometry analysis of the crude reaction mixtures showed the presence of dihydrophosphindole **2** and dihydrophthalimide **6** with molecular weights of $m/z = 382$ and 239, respectively.

On the basis of the precedents [4], a mechanism involving a five-coordinate adduct **8**, giving by fragmentation the tautomeric form **9** of the H-phosphinate **3** or **7** seemed to be effective (Scheme 3). We were successful in obtaining new evidence for the involvement of the addition–elimination (AE) reaction path during the photochemical reaction of phosphanorbornenes and alcohols. We assumed that the phosphanorbornenes (**1**, **4**, and **5**) should select between the primary and the secondary alcohols if the AE reaction path is effective, whereas with the elimination–addition (EA) mechanism there should not be a significant discrimination because the reactive oxophosphine (ArPO) is not expected to differentiate between the alcohols to a large extent. The photolysis of phosphole oxide dimer **1** was carried out in the presence of an equimolar mixture of methyl alcohol and isopropyl alcohol. As we had expected, there was a reasonable selection between the alcohols; methyl alcohol was more reactive than the isopropyl alcohol, as the methyl phosphinate (**3a**) predominated over the isopropyl ester (**3c**) (71 vs. 29%, Scheme 4).

Our other idea was to use an equimolar mixture of a P-phenyl and a P-triisopropylphenyl phosphanorbornene (**10** and **11**) in the photochemical reaction with methyl alcohol. In the case of the AE mechanism, the methyl alcohol was assumed to select between the phenyl- and the trialkylphenyl-phosphanorbornenes in favor of the phenyl derivative; the EA reaction path did not promise a significant discrimination. The photolysis of the equimolar mixture of **10** and **11** in the presence of methyl alcohol was interrupted several times before completion, and the mixture was analyzed by ^{31}P NMR. We found that the phenylphosphanorbornene **10** was consumed faster than the trialkylphenyl derivative **11** (Scheme 5). The above observations on the different kinds of competitive reactions are consistent with the intermediacy of a pentacoordinate P-intermediate, as the significant impact of the steric hindrance from both the alcohol and the phosphanorbornene components of the reaction can only be explained in this case.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4 MHz. Chemical shifts are downfield relative to 85% H_3PO_4. Gas chro-

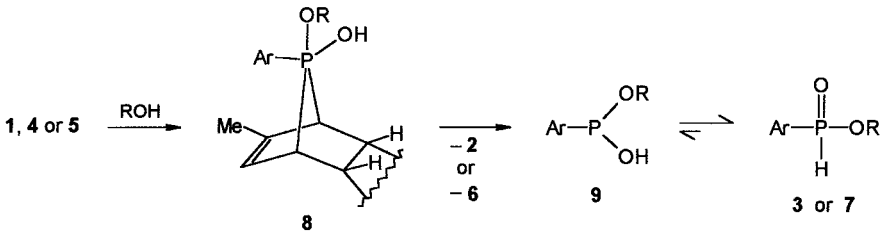
TABLE 1 Photolysis of P-Aryl Phosphanorbornenes (**1, 2**, and **5**) in the Presence of Alcohols at Room Temperature[a]

Entry	*Starting material*	*ROH*	*Reaction time (h)*	*Product*	*Yield (%)*	δ_P ($^1J_{PH}$) (*Hz*)	δ_P*[lit]* ($^1J_{PH}$) *[lit]*	M^+_{found} (M^+_{calc})
1	**1**	MeOH	3.5	**3a**	96	27.8 (562.2)	26.9 [4] (551.0)	
2	**1**	EtOH	4	**3b**	91	24.3 (549.2)	23.6 [4] (549.1)	
3	**1**	iPrOH	4	**3c**	84	21.0 (546.9)		310.2062 (310.2061)
4	**4**	MeOH	3.5	**3a**	95	27.7	26.9 [4]	
5	**4**	EtOH	3.5	**3b**	89	24.5	23.6 [4]	
6	**5**	MeOH	4	**7a**	82[b]	32.3 (37%)		324.2211[c]
				7a′		30.7 (38%)		(324.2218)
				7a″		30.3 (25%)		

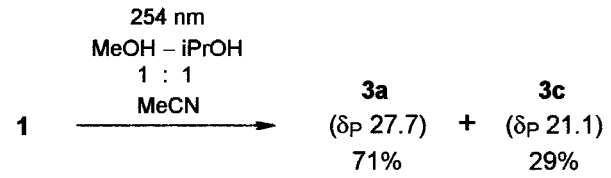
[a]See Experimental for the general procedure.
[b]Total yield.
[c]For the isomeric mixture.

TABLE 2 Relative Intensities (%) of the Major Fragments in the Mass Spectra of Compounds **3a**, **7a**, **7a′**, and **7a″**

Compound	M^+	$M - Me$	$M - R'$	$M - R' + H$	$M - R' - Me + H$	$M - P(O)(OMe)H$	$M - P(O)(OMe)H - Me + H$
3a	89	100	33	5			
7a	33	100	43	7	32		
7a′	24	29	100	50	91	23	4
7a″	4	25	6	20	24	5	100



SCHEME 3



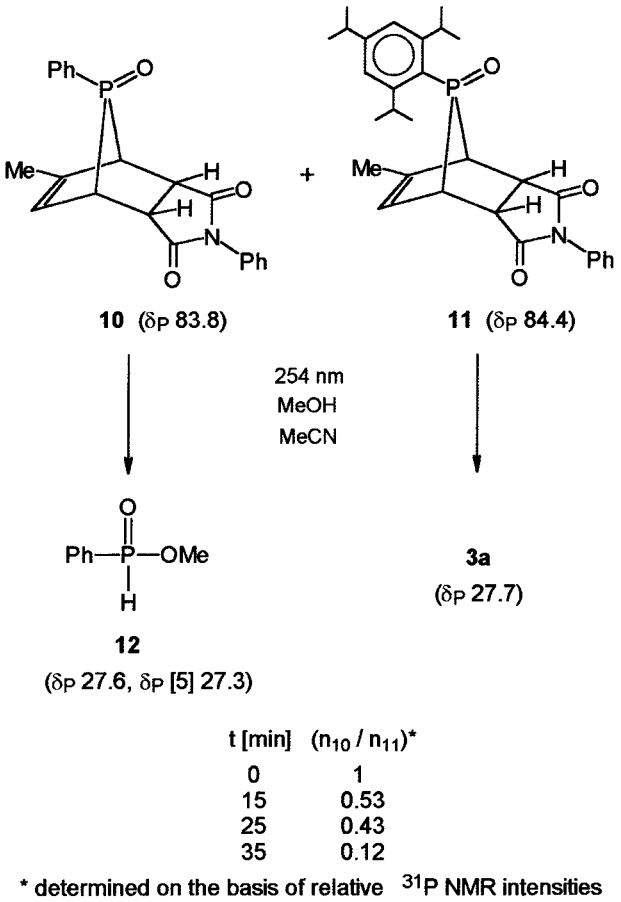
SCHEME 4

matography–mass spectrometry was performed on a Fisons GC 8000/MD 800 apparatus.

The phosphanorbornenes with *syn* aryl group to the double bond (**1**, **10**, and **11**) were prepared by the trapping of phosphole oxides as described earlier [6–8]. The phosphanorbornenes with anti aryl group to the double bond (**4** and **5**) were synthesized by the trapping of phospholes followed by oxidation at the phosphorus atom [8].

*General Procedure for the Synthesis of Aryl-H-phosphinates (***3a–c, 7a***)*

A solution of 0.32 mmol of the phosphanorbornene (**1**, **4**, or **5**) in 45 mL of dry acetonitrile and 4 mL (98.0 mmol) of methyl alcohol, ethyl alcohol or isopropyl alcohol was irradiated in a photochemical reactor with a mercury lamp (125 W) for 3.5–4 hours. Volatile components were removed in vacuo, and the residue so obtained was purified by column chromatography (silica gel, 3% methyl alcohol in chloro-



t [min]	$(n_{10} / n_{11})^*$
0	1
15	0.53
25	0.43
35	0.12

* determined on the basis of relative ^{31}P NMR intensities

SCHEME 5

form) to give the corresponding products (**3a–c**, **7a**) as shown in Table 1.

The Competitive Reaction of Methyl Alcohol and Isopropyl Alcohol with Phosphole Oxide Dimer **1**

The photochemical reaction of 0.2 g (0.32 mmol) of dimer **1** with 2.0 mL (49.0 mmol) of methyl alcohol and 3.8 mL (49.0 mmol) of isopropyl alcohol in 45 mL of acetonitrile was performed according to the general procedure to give a mixture of H-phosphinates **3a** and **3c** as shown in Scheme 4.

The Competitive Reaction of Phenylphosphanorbornene **10** *and Arylphosphanorbornene* **11** *with Methyl Alcohol*

The photochemical reaction of 4.0 mL (98.0 mmol) of methyl alcohol with 0.09 g (0.25 mmol) of phenylphosphanorbornene **10** and 0.12 g (0.25 mmol) of aryl derivative **11** was performed according to the general procedure to give a 1:1 mixture of H-phosphinates **12** and **3a**. Interrupting the reaction after 15, 25, and 35 minutes, the ratio of starting materials **10** and **11** was determined as shown in Scheme 5.

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