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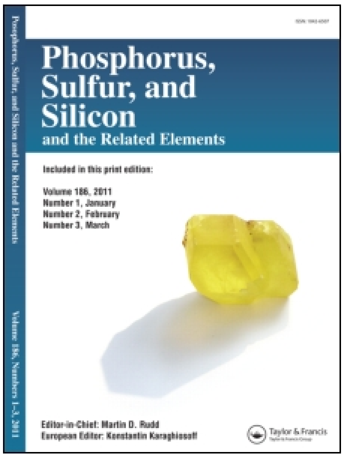

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Synthesis and Double Olefin Extrusion of 2,2,6,6-Tetraaryl-l,5-Dioxa-4λ^5-Phosphaspiro[3.3]Heptanes

Takayuki Kawashima; Rei Okazaki; Renji Okazaki

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SYNTHESIS AND DOUBLE OLEFIN EXTRUSION OF 2,2,6,6-TETRAARYL-1,5-DIOXA-4λ^5-PHOSPHASPIRO[3.3]HEPTANES

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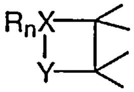
The title compounds were synthesized by cyclization and dehydration of the corresponding bis(β-hydroxyalkyl)phosphine oxides with Appel's reagent. Since these compounds were very moisture sensitive to hydrolyze to the starting bis(β-hydroxyalkyl)phosphine oxides except for tetrakis(4-nitrophenyl) derivative, their in-situ generation and thermolysis were carried out to give two molar equivalents of the corresponding olefins in good yield in sharp contrast to tetrakis(trifluoromethyl) derivative.

Keywords: Pentacoordinate 1,2-oxaphosphetanes, Wittig reaction, Thermolysis, Double olefin extrusion, 1,5-Dioxa-4λ^5-spiro[3.3]-heptanes

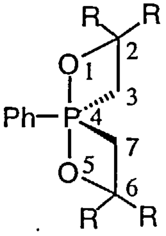
INTRODUCTION

In the course of our study on heteracyclobutanes **1**[1] bearing highly coordinate main group elements at the position adjacent to the heteroatom we have reported the syntheses and isolation of intermediates of the Wittig and Peterson-type reactions[2]. Recently we also achieved the synthesis of tetracoordinate and pentacoordinate 1,2-oxathietanes and oxirane formation reaction with retention of configuration[3]. From our interest in the influence of ring size on the stability of 1,2-oxaphosphetanes, we have reported the first example, **2**, of a stable pentacoordinate spirophosphorane with two 1,2-oxaphosphetane rings by introducing trifluoromethyl groups at the 4-position[4,5]. Unexpectedly, however, double olefin extrusion from **2** was unsuccessful, because of the electronic effect of the strong electron-withdrawing groups. We now report the synthesis and double olefin extrusion of 2,2,6,6-tetraaryl derivatives **3**.



1

X= P, Si^-, Ge^-, Sn^-,
S, Se
Y= O, NPh

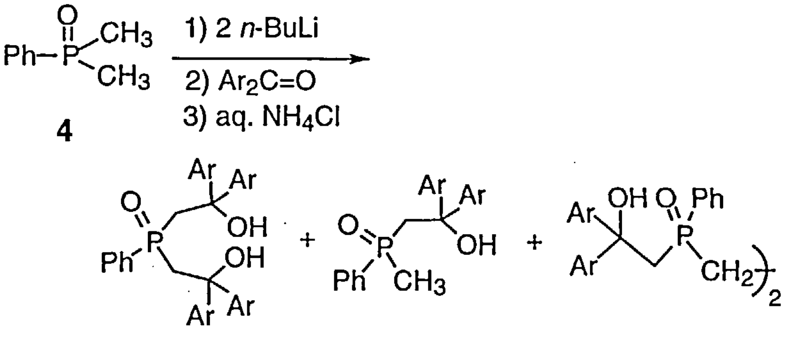


2: R= CF_3
3: R= Ar

RESULTS AND DISCUSSION

Sequential treatment of dimethylphenylphosphine oxide (**4**) with *n*-BuLi, benzophenone derivatives and then aqueous NH_4Cl gave bis(β-hydroxyalkyl)phosphine oxides (**5a-d**) along with monohydroxyalkyl derivatives **6** and diphosphine dioxide **7** (Scheme 1 and TABLE I).

Scheme 1



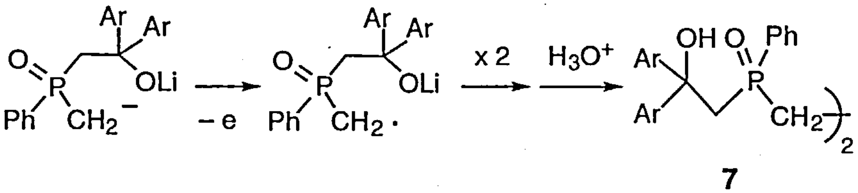
5 **6** **7**

TABLE I Yields of **5**, **6**, and **7**

	Ar	Yield[a)]/%		
		5	6	7
a:	Ph	87	7	–
b:	p-FC_6H_4	85	6	–
c:	p-ClC_6H_4	85	14	–
d:	p-$NO_2C_6H_4$	5	16	10

a) Isolated yields based on **4**.

In the case of the reaction with 4,4'-dinitrobenzophenone the yield of **5d** was quite low and diphosphine dioxide **7**, which seems to be formed by single electron transfer from the methylide of the mono adduct followed by homo-coupling reaction of methyl radicals thus formed, was also obtained.



7

Cyclization and dehydration of **5** by Appel's method[6], which was very effective for the synthesis of **2**, gave the corresponding **3** in high yields (by ^{31}P NMR). In the ^{31}P NMR the signal other than that due to triphenylphosphine oxide was observed at δ –39.1~ –40.1 (TABLE II), indicating the formation of pentacoordinate phosphoranes. Compounds **3** could not isolated except for 4-nitrophenyl derivative **3d**[7] (61% (isolated yield)), because they were moisture-sensitive to hydrolyze to **5**. Very recently, we have succeeded in the synthesis, isolation, and crystallographic analysis of all diastereoisomers of tetrakis(p-chlorophenyl)dimethyl derivatives by taking advantage of stabilizing effect of an electron-releasing methyl group at the carbons adjacent to the phosphorus atom[8]. These results suggest that introduction of more electron-withdrawing group than *p*-nitrophenyl group at the β-position or introduction of electron-releasing group at the α-position is very effective for the isolation of this type of species.

In-situ generation and thermolysis of **3** were carried out in

Scheme 2

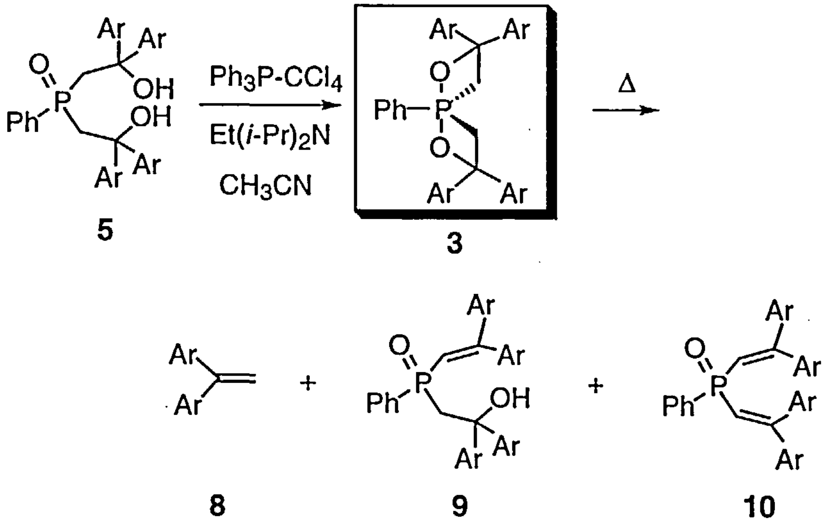


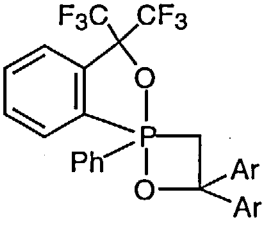
TABLE II In-situ generation and thermolysis of **3**

5	Ar	δ_P	$3/\delta_P$	Temp/°C	Time/h	Yield[a)]/%		
						8	**9**	**10**
a	Ph	45.9	−39.3	55	10	178[b)]	1	3
b	*p*-FC_6H_4	45.4	−40.9	55	10	178	–	10
c	*p*-ClC_6H_4	45.6	−40.6	55	10	169	–	10
d	*p*-$NO_2C_6H_4$	44.6	−39.1	100	1	153[c)]	–	–

a) Isolated yields (mol%) based on **5**. b) Conversion yield. **5a** (5%) was recovered. c) Unidentified products were obtained.

CH_3CN to give the corresponding olefins **8** along with byproducts **9** and **10** (Scheme 2 and TABlE II).

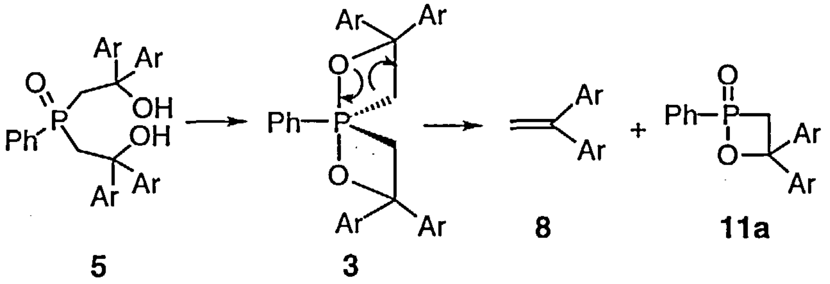
Judging from the yields of the products it can be concluded that tetraaryl derivatives **3** undergo double olefin extrusion to give two molar equivalents of the olefins in sharp contrast to **2**. The yield of the olefin seems to slightly decrease as the substituent of the para-position becomes more electron-withdrawing and in the case of the *p*-nitrophenyl derivative more drastic conditions were necessary, indicating the substituent effect similar to that reported for **1a**[1b].

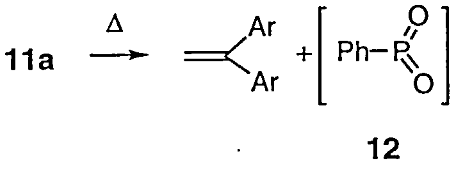


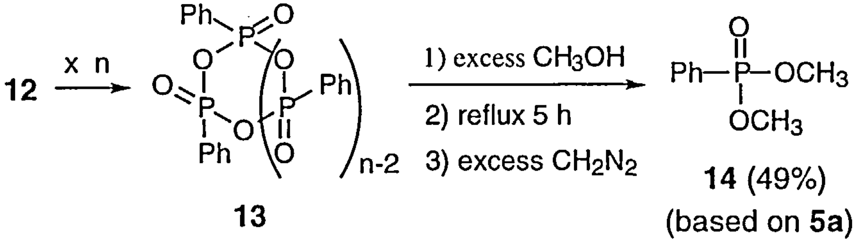
1a

$$\log (k/k_0) = -0.709\ (2\,\sigma_p{}^+)\ (r = 0.999)$$

The plausible mechanism of the double olefin extrusion is shown as follows: a Wittig-type olefination of **3** gives the olefin and tetracoordinate 1,2-oxaphosphetane **11a**, which is known to give the corresponding olefin and metaphosphonate **12** under the reaction conditions[9]. Metaphosphonate **12** rapidly undergoes oligomerization to afford **13**.

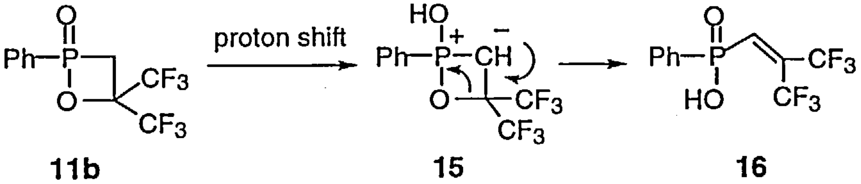






In fact, the formation of oligomer **13** was confirmed by the methanolysis of the reaction mixture using **5a**, followed by the reaction with diazomethane giving the corresponding dimethyl phenylphosphonate (**14**).

The difference in the reactivity between compounds **2** and **3** is probably attributable to the acidity of the methylene proton α to the phosphorus of intermediary tetracoordinate 1,2-oxaphosphetanes. In the case of **2** the proton of **11b** became more acidic by electron-withdrawing trifluoromethyl groups, so that intramolecular or intermolecular proton shift took place to form ylide **15**, which rapidly underwent ring opening to afford vinyl phosphinic acid **16**, while a Wittig-type olefination of **11a** occurred readily, because the proton acidity of **11a** was not enough for deprotonation by the phosphoryl group.



Acknowledgments

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