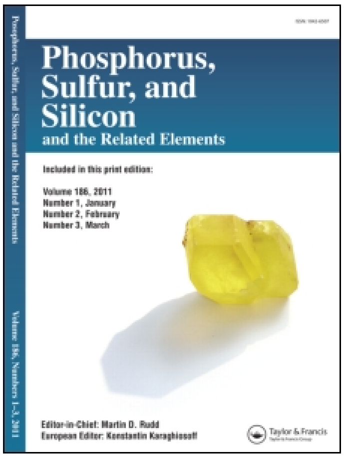
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Preparation of 5-Halo-2,2'-Bipyridyls

Yuzuru Uchida[a]; Ryuji Kajita[a]; Yoshikane Kawasaki[a]; Shigeru Oae[b]
[a] Department of Applied Chemistry, Osaka Institute of Technology, Osaka [b] Institute of Heteroatom Chemistry, Osaka-fu, Japan

To cite this Article Uchida, Yuzuru , Kajita, Ryuji , Kawasaki, Yoshikane and Oae, Shigeru(1994) 'Preparation of 5-Halo-2,2'-Bipyridyls', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 405 — 409

To link to this Article: DOI: 10.1080/10426509408021878

URL: http://dx.doi.org/10.1080/10426509408021878

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

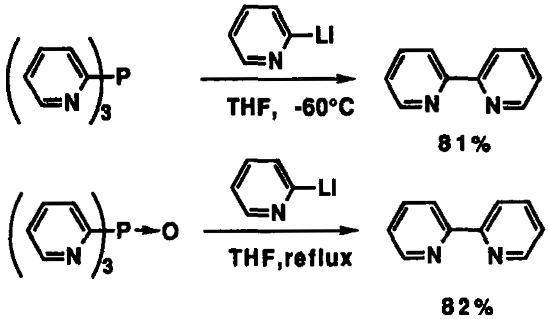
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 405–409
Reprints available directly from the publisher
Photocopying permitted by license only

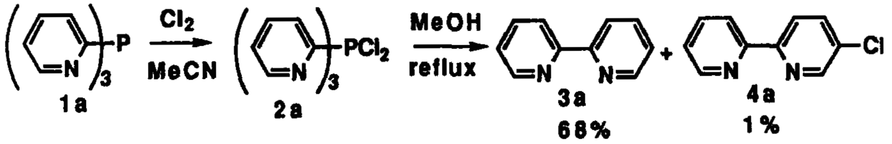
PREPARATION OF 5-HALO-2,2'-BIPYRIDYLS

Yuzuru Uchida, Ryuji Kajita, and Yoshikane Kawasaki, Department of Applied Chemistry, Osaka Institute of Technology, Osaka 535
Shigeru Oae, Institute of Heteroatom Chemistry, 2509 Hirao, Mihara-cho, Minamikawachi-gun, Osaka-fu 578 Japan.

Earlier, we have shown that treatment of tris(2-pyridyl)phosphine1) or tris(2-pyridyl)phosphine oxide2) with 2-pyridyllithium resulted in the formation of ligand coupling products, namely 2,2'-bipyridyl, as shown below.



Treatment of tris(2-pyridyl)phosphine (**1a**) with gaseous chlorine in acetonitrile afforded tris(2-pyridyl)phosphine dichloride (**2a**) which reacted further with refluxing methanol gave not only the ligand coupling product (**3a**) but also a small quantity of 5-chloro-2,2'-bipyridyl (**4a**) as shown below.



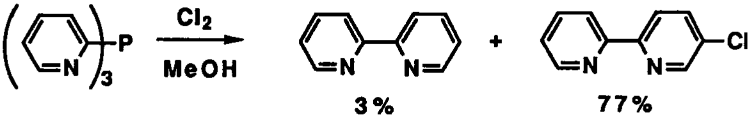
When the reaction was carreied out in acetonitrile in the presence of a small amount of methanol, the yield of **4a** increaced to 42% . This is intriguing and hence we started look into the reaction. The effect of protic solvent was first thought to be responsible. Thus, the various alcohols were tested (see TABLE 1).

TABLE 1 Products formed with small amount of water or alcohols

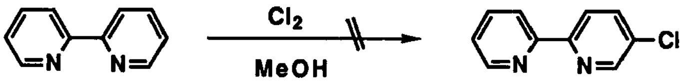
Alcohol	ROH /1a	Reaction time	Product Yeild (%) [a] 3a	4a
MeOH	3	16 h	40	42
EtOH	3	5 days	5	46
t-BuOH	3	4 h	6	25
	10	4 h	2	34
H_2O	10	4 h	3	76

a) Determined by GLC

Treatment of tris(2-pyridyl)phosphine with chlorine in methanol afforded the chlorinated 2,2'-bipyridyl as a major coupling product.

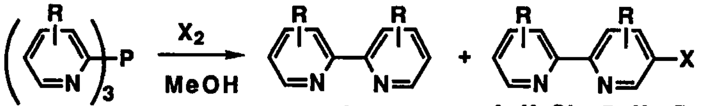


Of course, chlorination did not proceed by treating 2,2'-bipyridyl with chlorine in methanol under the same conditions.



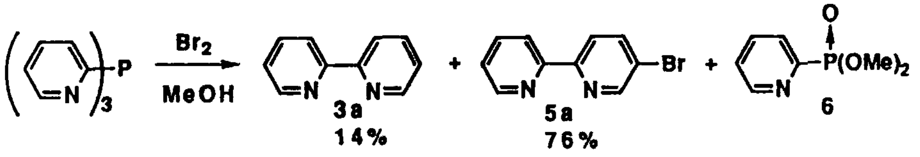
The reaction would proceed the path A and B (see Scheme 1).

Likewise, the additions of bromine into the methanol solution of tris(2-pyridyl)phosphine at room temperature gave 5-bromo-2,2'-bipyridyl (**5a**) along with 2,2'-bipyridyl, a normal coupling product. Phosphines, bearing methyl-substituted pyridines reacted similarly. The results in the following reaction are summarized in TABLE 2.

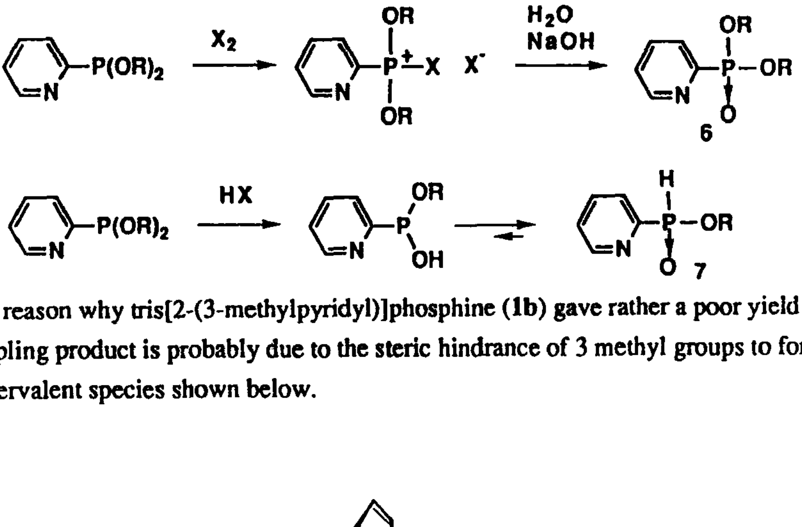


1 3 4; X=Cl, 5; X =Br

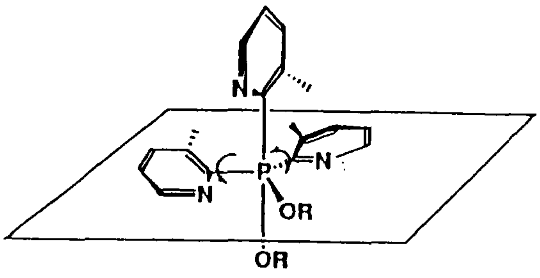
In the reaction between tris(2-pyridyl)phosphine and bromine in methanol we found the formation of dimethyl 2-pyridylphosphonate (6) in the following manner.



The formation of 6 and 7 could be suggested in the following reactions.



The reason why tris[2-(3-methylpyridyl)]phosphine (1b) gave rather a poor yield of the coupling product is probably due to the steric hindrance of 3 methyl groups to form the hypervalent species shown below.

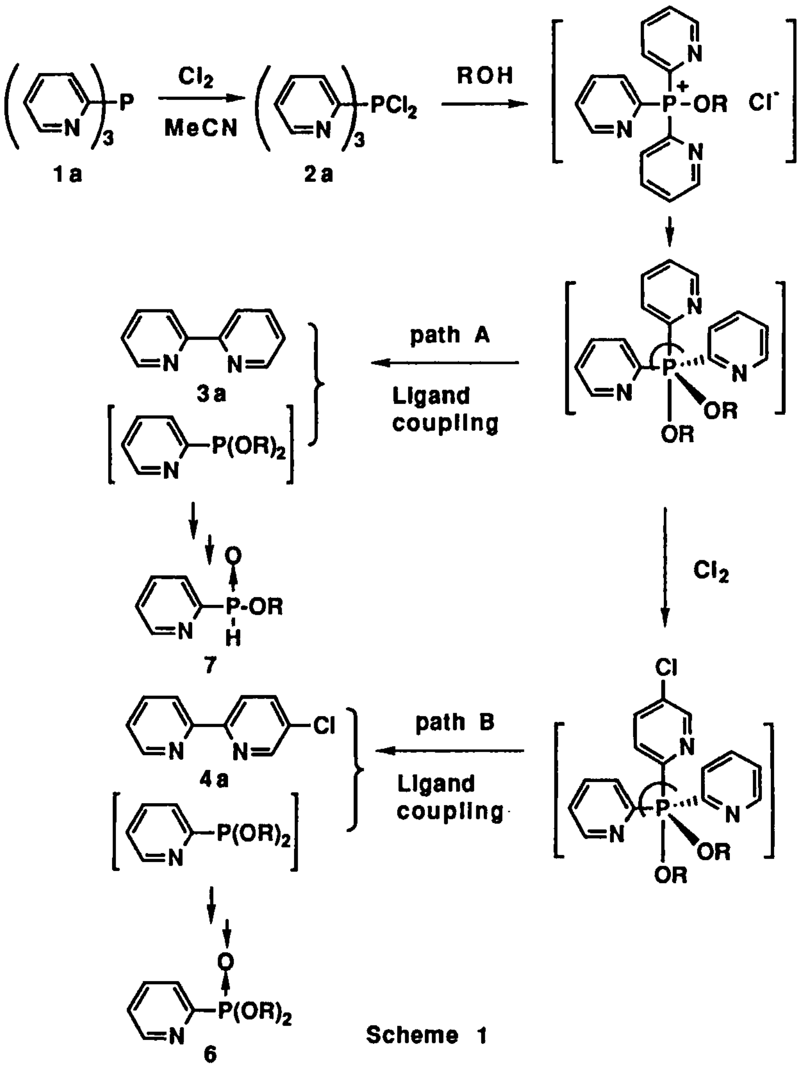


The reactions of other electrophile are also quite interesting. The following NMR spectra would indicate the presence of D in the NMR charts shown below.

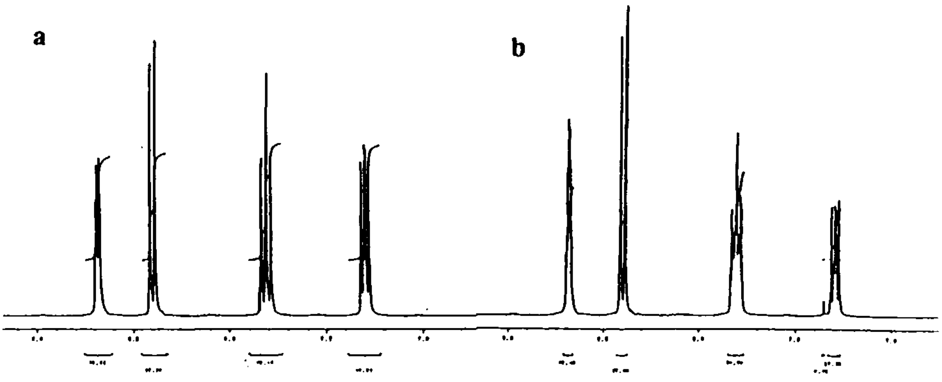
TABLE 2 Reaction of phosphines (**1**) with chlorine or bromine in methanol

	R	X	Product Yield (%)[a)]					
1a	H	Cl	**3a**	3	5[b)]	**4a**	77	58[b)]
1b	3-Me	Cl	**3b**	2		**4b**	11	
1c	4-Me	Cl	**3c**	6		**4c**	63	
1d	6-Me	Cl	**3d**	22	12[b)]	**4d**	73	58[b)]
1e	6-Ph	Cl	**3e**	-	19[b)]	**4e**	-	3[b)]
1f	6-Br	Cl	**3f**	-	0[b)]	**4f**	-	0[b)]
1a	H	Br[c)]	**3a**	14		**5a**	76	
1c	4-Me	Br[c)]	**3c**	36		**5c**	48	
1d	6-Me	Br[c)]	**3d**	22		**5d**	69	

a) Determined by GLC. b) Isolated yield. c) Phosphine : Br_2 = 1: 3

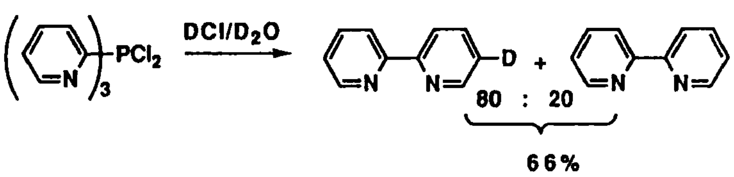


Scheme 1

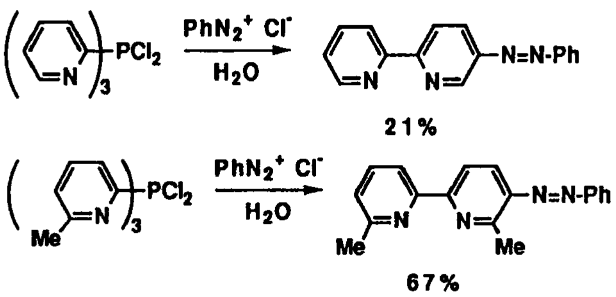


NMR pectra of (a) 2,2'-bipyridyl and (b) a mixture of 5-deuterio-2,2'-bipyridyl and 2,2-bipyridyl (80 : 20)

Unfortunately, the separation of the deuterated and the undeuterated 2,2-bipyridyl could not be acheaved, however, the ratio was estimated as shown below.



Another example of electrophilic substitution is the diazocoupling reaction . Two such examples are shown below.



REFERENCES

1) Y. Uchida, M. Kawai, H. Masauji, and S. Oae, *Heteroatom Chem. 4*, 1993, 421

2) Y. Uchida, H. Kozawa, and S. Oae, *Tetrahedron Lett.*, *30*, 1989, 6365; Y. Uchida. K. Onoue, N. Tada, F, Nagao, H. Kozawa, and S. Oae, *Heteroatom Chem.*, *1*, 1990, 295.