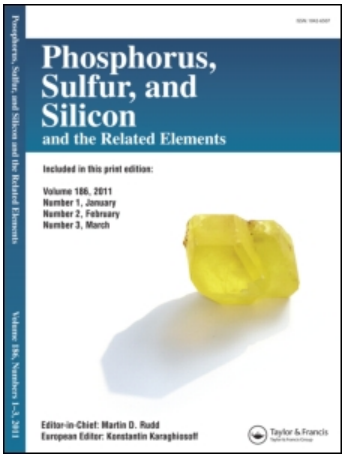

Phosphorus, Sulfur, and Silicon and the Related Elements

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

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To cite this Article Yoshifuji, Masaaki , Toyota, Kozo and Yoshimura, Hideki(1993) 'Reaction of Dichlorocarbene with Some Organo-Phosphorus Compounds in Low Coordination States', Phosphorus, Sulfur, and Silicon and the Related Elements, 76: 1, 67 — 70
To link to this Article: DOI: 10.1080/10426509308032360
URL: http://dx.doi.org/10.1080/10426509308032360

Phosphorus, Sulfur, and Silicon, 1993, Vol. 76, pp. 67–70
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REACTION OF DICHLOROCARBENE WITH SOME ORGANOPHOSPHORUS COMPOUNDS IN LOW COORDINATION STATES

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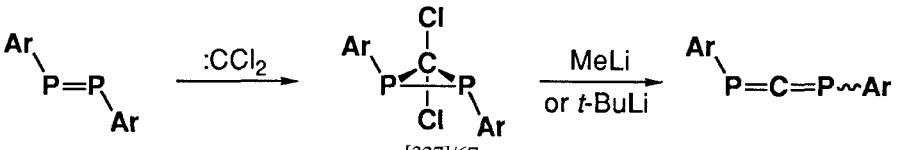
Abstract The reactions of dichlorocarbene with some organophosphorus compounds in low coordination states such as diphosphenes, phosphaethylenes, phosphaallenes, phosphabutatrienes, and phosphaalkynes were carried out.

INTRODUCTION

We have been successful in isolating organophosphorus compounds in low coordination states[1] by introducing a bulky substituent such as 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar) as a protecting auxiliary.[2] Kinetically stabilized phosphorus compounds thus obtained include diphosphenes,[2] phosphaethylenes,[3] phosphaallenes,[4] diphosphaallenes,[5] phosphabutatrienes,[6,7] and phosphaalkynes.[8,9] Moreover, we have been interested in the structures and reactivities of multiple bonds involving phosphorus atom(s) of coordination numbers 2 and 1. We describe here our experimental results on the reactions of dichlorocarbene with several phosphorus compounds in low coordination states.

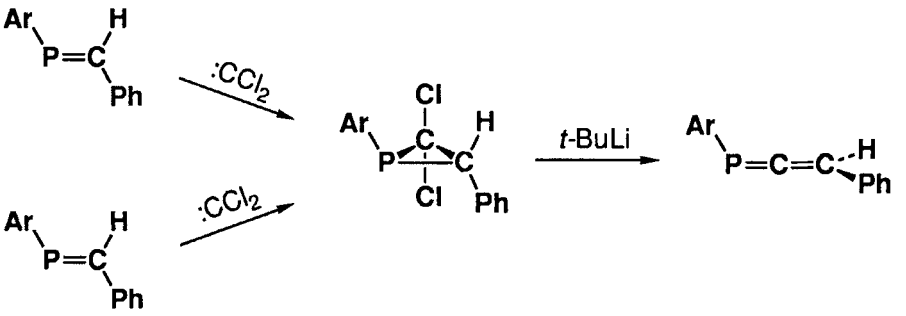
Reaction of Dichlorocarbene with Diphosphenes

The reaction of dichlorocarbene with diphosphenes[10,11] gave 3,3-dichlorodiphosphiranes which were converted to the corresponding 1,3-diphosphaallenes with methyllithium or *t*-butyllithium and a typical example for ArP=PAr is shown as follows.



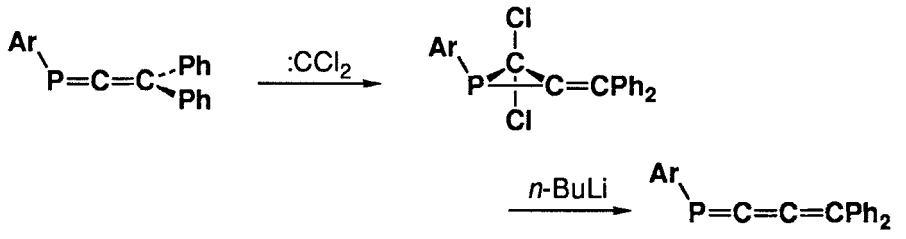
Reaction with Phosphaethylenes

The reaction of dichlorocarbene either with (*E*)- or (*Z*)-2-phenylphosphaethylene gave *trans*-phosphirane[10] which could be converted to 1-phosphaallene with *t*-butyllithium at low temperature, while methyllithium gave an alkylated product, 3-phospha-1-butyne. On the other hand, 2,2-diphenylphosphaethylene afforded a phosphaindane derivative carrying 1-chloro-2,2-diphenylethenyl group in the reaction with dichlorocarbene.



Reaction with Phosphaallenes

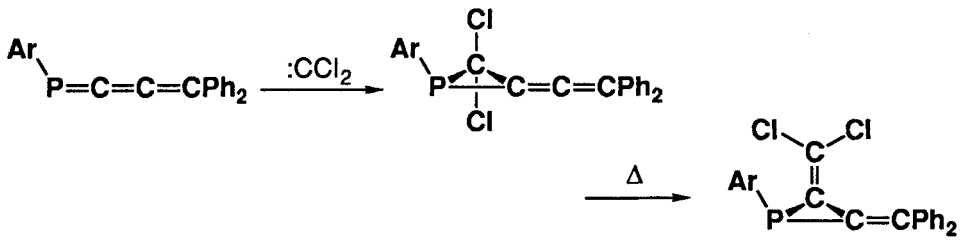
The reaction of 1-phosphaallene with dichlorocarbene gave 2,2-dichloro-3-diphenylmethylenephosphirane.[12] The phosphirane was successfully converted to 4,4-diphenyl-1-phosphabutatriene[13] with *n*-butyllithium at low temperature while *t*-butyllithium gave 1-phospha-2-butynes having one *t*-butyl group at either phosphorus atom.



Reaction with Diphosphabutatriene

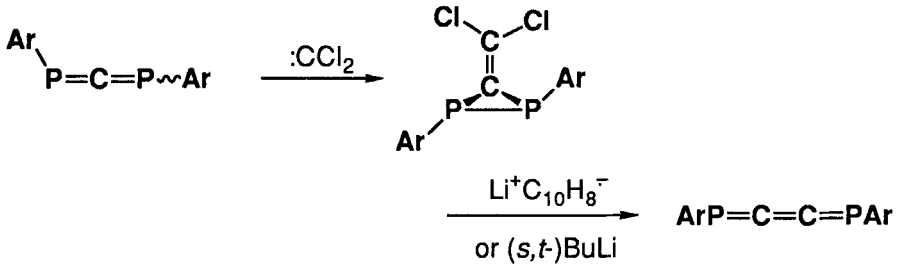
The reaction of 1-phosphabutatriene gave ethenylidenephosphirane[14] and the resulting phosphirane was transformed to a phospha-[3]-radialene, 2,3-dimethylenephosphirane,[15] on heating in

refluxing hexane, the structure of which was confirmed by the X-ray crystallographic analysis.



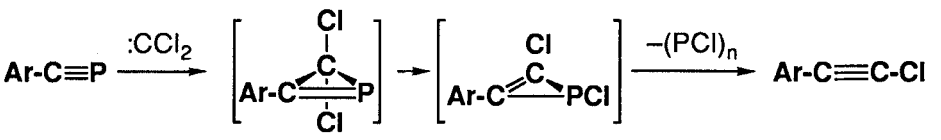
Reaction with Diphosphaallenes

The reaction of 1,3-diphosphaallene gave 3-dichloromethylene-1,2-diphosphirane[13] instead of the expected phosphinidenephosphirane. Furthermore the diphosphirane thus obtained was successfully converted to 1,4-diphosphabutatriene[14] with lithium naphthalenide, while the reaction with *t*- or *s*-butyllithium gave the corresponding butylated 1,4-diphospha-2-butyne. The structure of the methylenediphosphirane was unambiguously confirmed by the X-ray analysis.



Reaction with Phosphaalkynes

The reaction of dichlorocarbene with phosphaalkyne of coordination number 1, ArC≡P, gave ethynyl chloride probably *via* phosphirene intermediates, followed by elimination of $(PCl)_n$. Some other chloro- or bromocarbenes also gave similar reaction products.[17]



CONCLUSION

Thus the reactions or dichlorocarbene with organophosphorus compounds in low coordination states gave various kinds of interesting compounds some of which were useful in preparation of expanded phosphacumulenes with alkyllithium reagents or an electron transfer reagent.

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