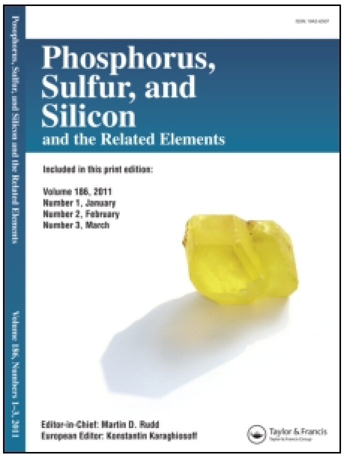
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

New Phosphaalkenes with Alkylthio and Fluorenylidene Groups. Synthesis and Properties

O. I. Kolodiazhnyi[a]; I. V. Shevtchenko[a]; V. P. Kukhar[a]
[a] Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, USSR

To cite this Article Kolodiazhnyi, O. I. , Shevtchenko, I. V. and Kukhar, V. P.(1987) 'New Phosphaalkenes with Alkylthio and Fluorenylidene Groups. Synthesis and Properties', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 433 — 436

To link to this Article: DOI: 10.1080/03086648708080613

URL: http://dx.doi.org/10.1080/03086648708080613

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 and Sulfur, 1987, Vol. 30, pp. 433–436
Photocopying permitted by license only

© 1987 Gordon and Breach Science Publishers, Inc.
Printed in the United Kingdom

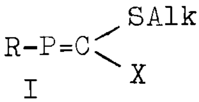
NEW PHOSPHAALKENES WITH ALKYLTHIO- AND FLUORENILIDENE GROUPS. SYNTHESIS AND PROPERTIES

O.I.KOLODIAZHNYI, I.V.SHEVTCHENKO, V.P.KUKHAR'
Institute of Organic Chemistry, Academy of
Sciences of the Ukrainian SSR, Kiev-252094, USSR

Abstract Synthesis and properties of new phosphaalkenes having different functional substituents at phosphorus and carbon atoms are discussed.

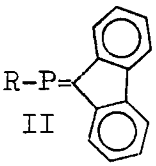
Downloaded At: 07:46 30 January 2011

New phosphaalkenes (type I and II) containing alkylthio- and fluorenilidene groups at carbon atom of the P=C bond were obtained in order to study their stability and reactivity.

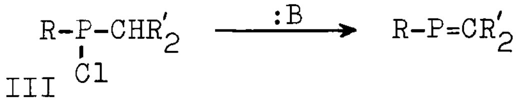


I

X = SAlk, $SiMe_3$

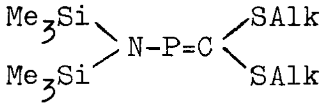


II



$$\underset{\mathrm{III}}{\mathrm{R{-}\underset{Cl}{P}{-}CHR'_2}} \xrightarrow{:B} \mathrm{R{-}P{=}CR'_2}$$

These compounds were prepared by treating the correspondent chlorophosphines (III) with bases (triethylamine, DBU or lithium hexamethyldisilazane).[1] The phosphaalkenes (I) are stabilized by bulky substituents at sulfur and, especially, at phosphorus atom. P-Bis-(trimethylsilyl)amino-C-bis(methylthio)phosphaethylene (IV) was found to be the most stable compound. Heating to 150 °C does not lead to its decomposition.

IV 

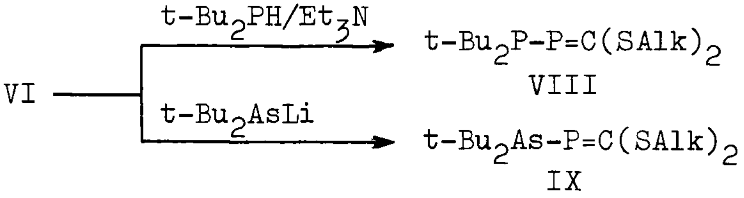
$(Me_3Si)_2N\text{-}P{=}C(SAlk)_2$

$\delta_P = 260$ ppm

Dichlorophosphines (V) were dehydrochlorinated by triethylamine at 0°C to give P-chloro-C-bis(alkylthio)-phosphaethylenes (VI) which are stable in solution below 0°C. They are key synthones for the preparation of various phosphaalkenes (VII) having different functional substituents at phosphorus. The chlorine atoms in these compounds are readily substituted by nucleophiles with P=C bond being preserved.[1]

$$\underset{V}{Cl_2P\text{-}CH(SAlk)_2} \xrightarrow{Et_3N} \underset{VI}{Cl\text{-}P{=}C(SAlk)_2} \xrightarrow{Nu^-} \underset{VII}{Nu\text{-}P{=}C(SAlk)_2}$$

The reaction of chlorophosphaalkenes with phosphines or arsines leads to the P-P and As-P substituted phosphaalkenes (VIII) and (IX).[2]



$$VI \xrightarrow{t\text{-}Bu_2PH/Et_3N} \underset{VIII}{t\text{-}Bu_2P\text{-}P{=}C(SAlk)_2}$$

$$VI \xrightarrow{t\text{-}Bu_2AsLi} \underset{IX}{t\text{-}Bu_2As\text{-}P{=}C(SAlk)_2}$$

The stability of these new P-P and As-P phosphaalkenes increases substantially when alkylthio groups at carbon atom of the P=C bond are substituted by more bulky trimethylsilyl radicals. The reactions of phosphaalkenes (X) with halogen alkanes or acetyl chloride are accompanied by P-P bond cleavage and P-halogenophosphaethylenes (XI) are obtained.

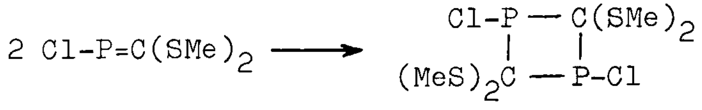
$$\underset{X}{t\text{-}Bu_2P\text{-}P{=}C(SiMe_3)_2} \xrightarrow{RX} \underset{XI}{X\text{-}P{=}C(SiMe_3)_2} + t\text{-}Bu_2P\text{-}R$$

R = Me, Et, Ac; X = I, Br, Cl

Downloaded At: 07:46 30 January 2011

The reaction of the compound (X) with CBr_4 results in formation of tribromomethylphosphaethylene (XI, X = CBr_3).

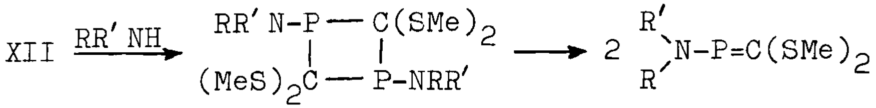
P-Chloro-C-bis(methylthio)phosphaethylene readily dimerizes to give dimer (XII). Its "head-to-tail" structure was confirmed by ^{13}C NMR spectrum.



$$2\ \text{Cl-P=C(SMe)}_2 \longrightarrow \begin{array}{ccc}\text{Cl-P} & \text{—} & \text{C(SMe)}_2\\ | & & | \\ \text{(MeS)}_2\text{C} & \text{—} & \text{P-Cl}\end{array}$$

XII

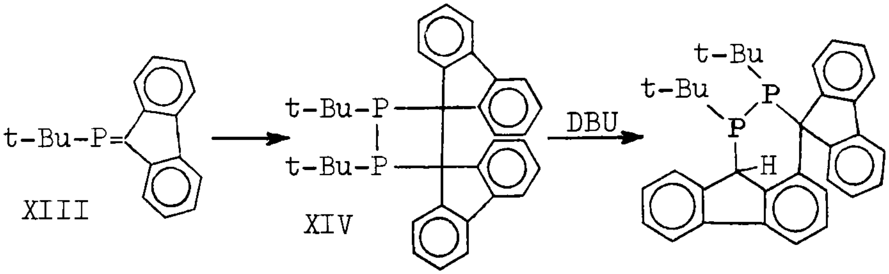
This dimer can participate in reactions of nucleophilic substitution with dimeric or monomeric products being formed depending on the substituent volume. The introduction of bulky substituents destabilizes the four-membered cycle structure and favours the formation of the monomeric phosphaalkenes.



$$\text{XII} \xrightarrow{\text{RR}'\text{NH}} \begin{array}{ccc}\text{RR}'\text{N-P} & \text{—} & \text{C(SMe)}_2\\ | & & | \\ \text{(MeS)}_2\text{C} & \text{—} & \text{P-NRR}'\end{array} \longrightarrow 2\ \begin{array}{l}\text{R}'\\ \quad\text{N-P=C(SMe)}_2\\ \text{R}'\end{array}$$

R, R = t-Bu, Me_3Si

The stability of the fluorenylidenephosphines (II) prepared by dehydrochlorination of corresponding chlorophosphines with bases changes in a wide range. P-tert-Butylfluorenylidenephosphine (XIII) is unstable and readily undergoes "head-to-head" cycloaddition to give dimer (XIV).^{3}

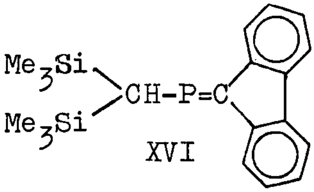


XIII XIV XV

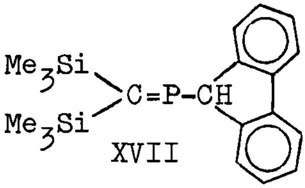
Downloaded At: 07:46 30 January 2011

Downloaded At: 07:46 30 January 2011

In the presence of catalytic amounts of DBU the dimer (XIV) easily rearranges into 1,2-diphosphorine (XV). The structure of the compounds (XIV, XV) was determined by the X-ray diffraction analysis. The transformation of the dimer (XIV) to the diphosphorine was also observed in its reaction with methyl iodide or with oxygen. P-Bis(trimethylsilyl)methyl-fluorenylidenephosphine (XVI) turned out a stable compound. We prepared its isomer (XVII) and investigated the prototropic migration in CH-P=C system of these compounds.[4]



XVI



XVII

At 20 °C the compounds (XVI) and (XVII) do not undergo mutual conversion. But in the presence of bases the isomerization of the type (XVI—XVII) becomes possible. For example, 1% of DBU results in fast transformation of (XVII) into (XVI). Triethylamine appears to be too weak base to catalyze the isomerization.

REFERENCES

1. V.P.Kukhar', I.V.Shevtchenko, O.I.Kolodiazhnyi, Zh. Obshch. Khim., 55, 264 (1985).
2. O.I.Kolodiazhnyi, I.V.Shevtchenko, V.P.Kukhar', Zh. Obshch. Khim., 55, 1862 (1985).
3. O.I.Kolodiazhnyi, I.V.Shevtchenko, V.P.Kukhar', at al, Zh. Obshch. Khim., 53, 1233 (1983).
4. O.I.Kolodiazhnyi, I.V.Shevtchenko, V.P.Kukhar', Zh. Obshch. Khim., 55, 2214 (1985).