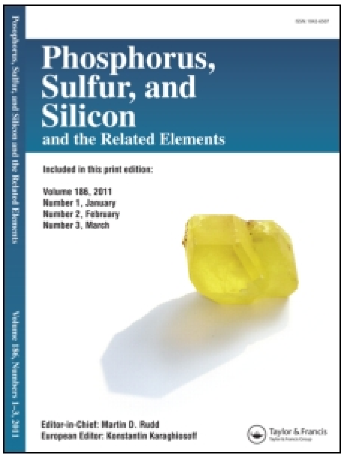
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Methylenephosphonium-ions: A New Class of Unsaturated Organophosphorus Compounds

Hansjörg Grützmacher[a]; Udo Heim[a]; Hartmuth Schönberg[a]; Hans Pritzkow[a]
[a] Anorganisch-chemisches Institut der Universität, W-6900, Heidelberg, F.R.G.

To cite this Article Grützmacher, Hansjörg , Heim, Udo , Schönberg, Hartmuth and Pritzkow, Hans(1993) 'Methylenephosphonium-ions: A New Class of Unsaturated Organophosphorus Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 76: 1, 21 — 24

To link to this Article: DOI: 10.1080/10426509308032348

URL: http://dx.doi.org/10.1080/10426509308032348

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.

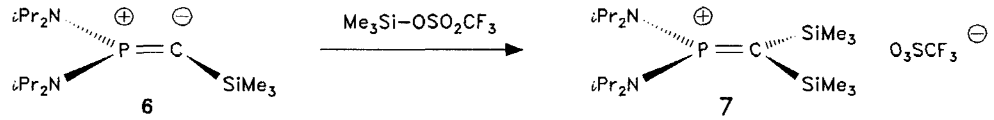
Phosphorus, Sulfur, and Silicon, 1993, Vol. 76, pp. 21–24
Reprints available directly from the publisher
Photocopying permitted by license only

METHYLENEPHOSPHONIUM-IONS: A NEW CLASS OF UNSATURATED ORGANOPHOSPHORUS COMPOUNDS

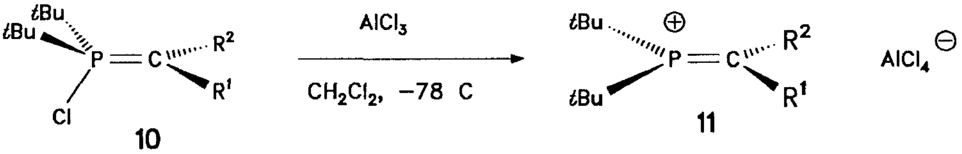
HANSJÖRG GRÜTZMACHER*, UDO HEIM, HARTMUTH SCHÖNBERG, HANS PRITZKOW
Anorganisch-chemisches Institut der Universität, Im Neuenheimer
Feld 270, W-6900 Heidelberg, F.R.G.

Abstract Methylenephosphonium ions, $R_2P=CR'_2{}^+$ X^-, could be prepared by either adding electrophiles to the carbene R_2P-C-R' (R = *i*Pr_2N, R' = $SiMe_3$) or abstracting chloride from P-halogenated ylides $R_2PCl=CR'_2$ (R = *t*Bu, R' = $SiMe_3$ or Aryl). Their structures and reactivity is discussed.

The chemistry of methylenephoshonium ions, $R_2P=CR'_2{}^+$ (**1**), is interesting under a varity of aspects. From an "inorganic" point of view they might be compared with isoelectronic silaethens, $R_2Si=CR'_2$ (**2**), and phosphino boranes, $R_2P=BR_2$ (**3**). The "organic" chemist will notice the iso(valence)electronic relationship of **1** with olefins, $R_2C=CR_2$ (**4**), and raise the question in how far an element from the third period will be able to stabilize a carbenium ion in view of the well established chemistry of iminium ions, $R_2N=CR_2{}^+$ (**5**).



While theoreticians have already found answers to these questions[1], experimentally, the existence of methylenephosphonium ions was only proven recently.[2] Adding an electrophilic reagent like Me_3Si-OSO_2CF_3 to the electron rich carbene **6** led to an isolable methylenephosphonium ion **7** which was characterized by an X-ray structure determination.[2a] However, the lone pairs of electrons located at the amino groups attached to phosphorus strongly disturb the π-bonding system in **7** which is not iso(valence)electronic to an olefin but has to be compared with the well known anionic tris(methylene)metaphosphates, $(R_2C)_3P^-$ (**8**), or - if a comparison to a purely organic molecule has to be made - with dianionic tris(methylene)methane dianion, $(H_2C)_3C^{2-}$ (**9**).[3] As in these typical Y conjugated π-bonding systems the iPr$_2$N and C(SiMe$_3$)$_2$ fragments in **7** distort strongly from molecular planarity and the observed bond shortening is not due to effective (p-p)π overlap but caused mainly by attractive electrostatic interactions.



	R^1	R^2
11a	H	SiMe$_3$
11b	SiMe$_3$	SiMe$_3$
11c	Ph	Ph
11d	Ph	p–tolyl
11e	Ph	m–tolyl
11f	Ph	o–tolyl

The obvious necessity to prepare methylenephosphonium ions **11a-f** which bear no substituents falsifying the P=C π-system was satisfied by abstracting a chloride ion from chlorinated ylides **10a-f**.[2b] This reaction is by no means trivial since the reagent $AlCl_3/CH_2Cl_2$ employed is known to be a rather strong one electron oxidizing reagent for compounds having a first vertical ionization potentials below 8 eV.[4] Indeed, even at low temperatures small amounts (<10%) of byproducts tBu$_2$PCl-CHR^{1}R^{2+} AlCl$_4^-$ (**13a-f**) which most likely stem from radical cations tBu$_2$PCl-CR^{1}R$^{2\cdot+}$ AlCl$_4^-$

(**12a-f**) are formed. In some cases these phosphonium salts **13** are the sole products (i.e.: R = *i*Pr$_2$N, R' = SiMe$_3$).[5]

In the NMR spectra of methylenephosphonium salts **11** resonances for the ^{13}C nucleus are observed at about 180 ppm in the range typical for methylenephosphanes RP=CR'$_2$. A signal for the ^{31}P nucleus is found approximately at 180 ppm if aryl groups are attached to the sp^2 carbon atom. A considerable downfield shift to about 250 ppm is observed if trimethylsilyl groups are bonded to the P=C π-bonding system. The values for the ^{13}C and ^{31}P NMR shifts are in accord with a "real" π-bond between the phosphorus and carbon atom. Interestingly, in low temperature NMR spectra of unsymmetrical **11a** only equivalent *t*Bu groups are observed. However, a solid state ^{13}C-CP/MAS-NMR spectrum clearly shows the expected signals for two inequivalent *t*Bu groups. Thus, a lower limit for the rotation barrier of $\Delta G^{\#} < 9$ kcal/mol can be estimated. Distinct from this observation, in the NMR spectra (^{13}C, ^{1}H) of unsymmetrical methylenephosphonium ions **11d** and **11f** no rotation around the P=C double bond up to 60°C is observed indicating a tight double bond with a rotation barrier above 20 kcal/mol which is in reasonable accord with calculated values.[3] Note, that all methylenephosphonium ions are extremely sensitive in solution, compound **11b** even decomposes in the solid state at -30°C to yet unknown products.

In spite of their sensitivity we could recrystallize compound **11a** and **11c** from hexane/methylene chloride solutions. Both were subsequently investigated by an X-ray analysis which proved the proposed structures. No close contacts between the anion and the cation were observed (non-distorted tetrahedron for the AlCl$_4^-$ anion). The configuration around the phosphorus atom is trigonal planar. The sterically encumbered cations of **11a,c** show a twist around the P=C bond of 11° and 20°, respectively. The bond distance of 1.67 Å is in the expected range of phosphorus carbon double bonds and does not differ from the one in the corresponding halogenated ylides **10**. It is instructive to compare the molecular structure of **11c** with the one of the tritylium salt Ph$_3$C$^+$ ClO$_4^-$ (**14**).[6] In the latter the phenyl rings are twisted by about 32° against the plane spanned by the central carbon atom and the three *ipso* carbon atoms of the aromatic rings. In **11c** this twist equals about 59° indicating that the electron deficiency at the carbenium atom is mainly compensated by the lone pair of electrons located at the phosphorus atom.

The reactivity of **11a - f** is typical for compounds having a phosphorus carbon double bond. While the amino substituted methylenephosphonium salt **7** does not react with dienes the methylenephosphonium salts **11** undergo exothermic reactions to yield either [4+2] cycloaddition products or products formed in ene reactions.

REFERENCES

1) a) L.L. Lohr, H.B. Schlegel, K. Morokuma, J. Phys. Chem., 88, 1981 (1984); b) F. Bernardi, A. Bottoni, A. Venturini, J. Am. Chem. Soc., 108, 5395 (1986); c) C. Schade, P. von Rague' Schleyer, J. Chem. Soc., Chem. Commun., 1987, 1399; d) M. Ehrig, H. Horn, C. Kölmel, R. Ahlrichs, J. Am. Chem. Soc., 113, 3701 (1991).

2) a) A. Igau, A. Bacereido, H. Grützmacher, H. Pritzkow, J. Am. Chem. Soc., 111, 6853 (1989); b) H. Grützmacher, H. Pritzkow, Angew. Chem. Int. Ed. Engl., 30, 709 (1991); c) H. Grützmacher, H. Pritzkow, Angew. Chem. Int. Ed. Engl., 31, 99 (1992).

3) a) R. Appel, E. Gaitzsch, F. Knoch, Angew. Chem. Int. Ed. Engl., 24, 589 (1985); b) W.W. Schoeller, J. Niemann, Phosphorus Sulfur, 46, 47 (1987); c) A. Gobbi, P.J. MacDougall, G. Frenking, Angew. Chem. Int. Ed. Engl., 30, 1001 (1991).

4) H. Bock, Angew. Chem. Int. Ed. Engl., 28, 1627 (1989) and lit. cited therein.

5) Erronously these compounds were described as methylenephosphonium ions: R. Appel, R. Schmitz, Chem. Ber., 116, 3521 (1983).

6) A.H. Gomes de Mesquita, C.H. MacGillavry, K. Eriks, Acta Cryst., 18, 437 (1965).