

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>

Synthesis and Reactivity of Unsaturated Bisphosphonium Salts

Henri-Jean Cristau^a; Gerald Duc^a; Lydie Labaudiniere^a; Francoine Pietrasanta^a; Francoise Plenat^a

^a Laboratoire de Chimie Organique ENSCM (ERA N° 610) 8, rue de l'Ecole Normale., MoN^opellier, France

To cite this Article Cristau, Henri-Jean , Duc, Gerald , Labaudiniere, Lydie , Pietrasanta, Francoine and Plenat, Francoise(1983) 'Synthesis and Reactivity of Unsaturated Bisphosphonium Salts', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 113 – 116

To link to this Article: DOI: 10.1080/03086648308075980

URL: <http://dx.doi.org/10.1080/03086648308075980>

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.

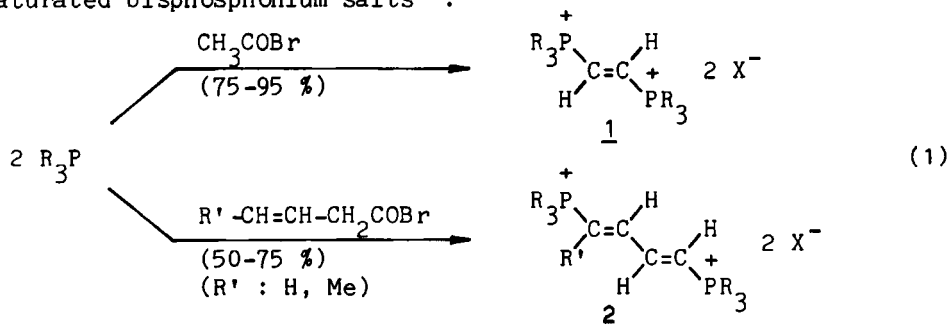
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any 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.

SYNTHESIS AND REACTIVITY OF UNSATURATED BISPHOSPHONIUM SALTS

HENRI-JEAN CRISTAU, GERALD DUC, LYDIE LABAUDINIERE, FRANCINE PIETRASANTA, FRANCOISE PLENAT
Laboratoire de Chimie Organique ENSCM (ERA n° 610)
8, rue de l'Ecole Normale. F-34075 Montpellier (France).

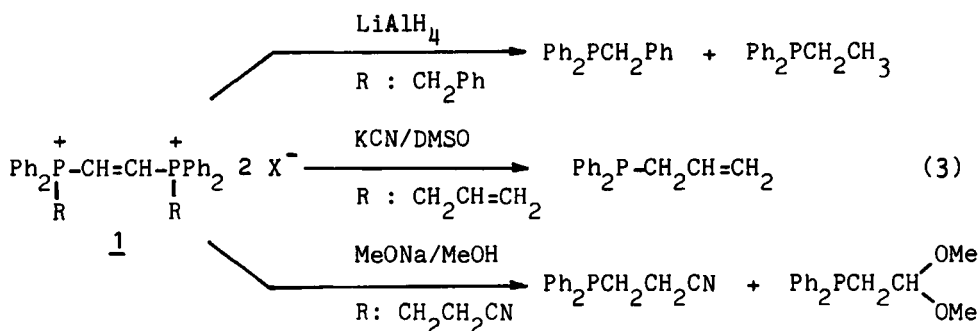
Abstract The synthesis of 1,2 vinylene bisphosphonium salts 1 has now been enlarged to the vinylogous 1,4-butadienylene bisphosphonium salts 2. The salts 2, a new class of unsaturated disalts, have also been prepared through a two-step isomerisation of acetylenic salts. New aspects of the reactivity of salts 1 and the comparative study of salts 2 (selective cleavage reactions of P-C bonds and reactions with nucleophiles having a mobile hydrogen) are described. This reactivity allows the preparation of new series of phosphonium salts substituted by heteroatomic groups.

In an earlier study¹, the reaction of tertiary phosphines with acetyl bromide has afforded a new synthesis of 1,2 vinylene bisphosphonium salts 1. We have now been able to enlarge through vinylogy this synthesis to the preparation of the higher homologs, the 1,4-butadienylene bisphosphonium salts 2, which are a new class of unsaturated bisphosphonium salts² :

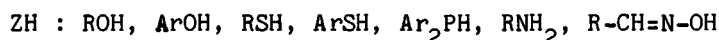
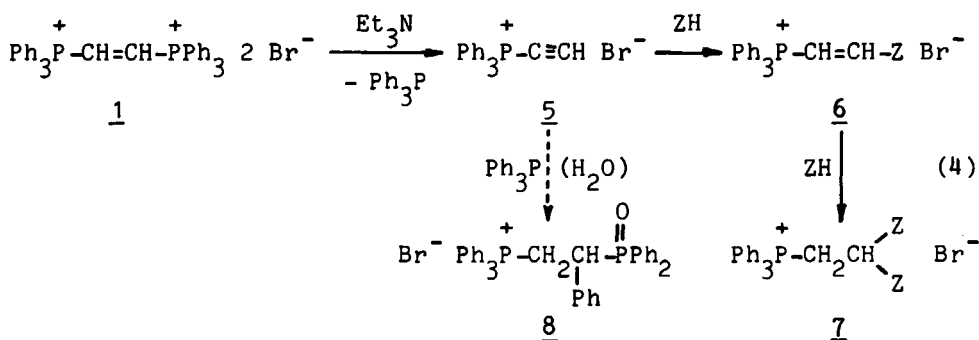


R_3P : PhPMe_2 , Ph_2PMe , $\text{Ph}_2\text{PCH}_2\text{Ph}$, $\text{Ph}_2\text{PCH}_2\text{CH}=\text{CH}_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CN}$
 nBu_3P , $(\text{PhCH}_2)_3\text{P}$, Ph_3P , $(p\text{-Me-C}_6\text{H}_4)_3\text{P}$, $(p\text{-MeO-C}_6\text{H}_4)_3\text{P}$

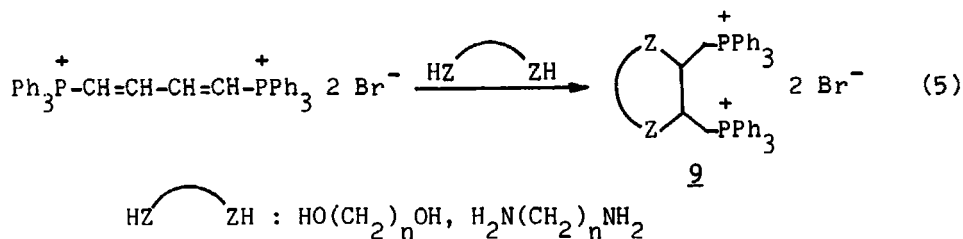
unsaturated bridge between the two phosphorus atoms⁴. The 1,2-vinylene bridge, particularly, includes a P^+-C bond which is till now among the most easy to cleave in the chemistry of phosphonium salts.



Towards nucleophilic agents bearing a mobile hydrogen ZH the disalts 1 and 2 behave differently, in basic medium, because of the greater instability of the unsaturated bridge for compound 1. Starting from disalt 1, we have recently shown⁵ that the reaction involves really the formation of an intermediate, the ethynylphosphonium salt 5, which accounts for the various end-products (the exact nature of the reagent ZH determines actually the reaction pathway to the phosphoniovinilation product 6, to the phosphonioethylation product 7 or to various secondary products like compound 8⁵) :



At the opposite, the disalts 2 react essentially as bis(vinylphosphonium)salts and give a double addition of compounds ZH (Equation (5)) :



It has already been shown that salts 6 are very good vinylation agents for alcohols and phenols⁶, while salts 7 give suitable Wittig's reagents for the n+1 homologation of aldehydes⁷. Salts 9 ought to be also useful for organic synthesis.

REFERENCES

1. H. Christol, H.-J. Cristau and J.-P. Joubert, Bull. Soc. Chim. Fr., 1421, 2263 and 2975 (1974).
2. H.-J. Cristau, G. Duc and H. Christol, Synthesis, 374 (1983).
3. K. Schloegl and H. Egger, Liebigs Annalen Chem., 676, 76 (1964).
4. H.-J. Cristau, L. Labaudinière and H. Christol, Phosphorus and Sulfur, 15, 359 (1983).
5. H.-J. Cristau, D. Bottaro, F. Plénat, F. Pietrasanta and H. Christol, Phosphorus and Sulfur, 14, 63 and 73 (1982).
6. H. Christol, H.-J. Cristau and M. Soleiman, Synthesis, 736 (1975).
7. H.-J. Cristau, H. Christol and D. Bottaro, Synthesis, 826 (1978).