

This article was downloaded by:

On: 28 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>

Lips--Syntheses of Phosphonium and Ammonium Liquid Ionic Phosphates

Jaimelee Iolani Cohen^a; Marie Thomas^a; Amir Rikin^a; Steve Castro^a; Valbona Behaj^a; Christopher Massone^a; Jennifer Gaillard^a; Sharon Lall^a; Robert Engel^a

^a Queens College, Graduate School, City University of New York, New York

Online publication date: 27 October 2010

To cite this Article Cohen, Jaimelee Iolani , Thomas, Marie , Rikin, Amir , Castro, Steve , Behaj, Valbona , Massone, Christopher , Gaillard, Jennifer , Lall, Sharon and Engel, Robert(2002) 'Lips--Syntheses of Phosphonium and Ammonium Liquid Ionic Phosphates', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 8, 2265 — 2266

To link to this Article: DOI: 10.1080/10426500213455

URL: <http://dx.doi.org/10.1080/10426500213455>

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.



LIPS—SYNTHESES OF PHOSPHONIUM AND AMMONIUM LIQUID IONIC PHOSPHATES

*Jaimelee Iolani Cohen, Marie Thomas, Amir Rikin,
Steve Castro, Valbona Behaj, Christopher Massone,
Jennifer Gaillard, Sharon Lall, and Robert Engel*
*Queens College the City University of New York and the
Graduate School of the City University of New York, New York*

(Received July 29, 2001; accepted December 25, 2001)

Using parent polycationic halide salts previously prepared by our laboratory, replacement of the anion to one that would allow the salt to be liquid at room temperature in the absence of water or other solvent medium was performed. Treatment of the polyammonium halides with aqueous hexafluorophosphoric acid resulted in the immediate formation of a solid material insoluble in water for which the ^1H and ^{13}C NMR spectra corresponded to those of the original halide salts. However, the ^{31}P NMR spectra indicated these to be mixtures of the (anticipated) hexafluorophosphate salt and simple phosphate salt. Evaporation of the remaining aqueous solution resulted in isolation of the pure phosphate salts as room temperature liquids—liquid ionic phosphates (LIPs) which exhibited water solubility and NMR spectra (^1H , ^{13}C , and ^{31}P) in total accord with the proposed structures. These represent a new category of nonaqueous ionic liquid which are water soluble and water unreactive. (The polycationic hexafluorophosphate salts could be purified by repeated washing with water and drying under high vacuum. These materials have not been investigated further in the present work.)

As this approach for the preparation of LIPs results in the formation of a significant amount of the water insoluble hexafluorophosphate species, as well as uses a highly corrosive and toxic reagent system, an alternative method for the preparation of LIPs was sought. Two alternative approaches toward the preparation of these polycationic phosphates have been developed. Treatment of the parent halide salts

Robert Engel, Department of Chemistry and Biochemistry, Queens College of the City University of New York and the Ph.D. Program in Chemistry, Graduate School of the City University of New York, 65-30 Kissena Boulevard, Flushing, New York, 11367.
E-mail: robert_engel@qc.edu

with DOWEX 2×8 in the phosphate from by a classical ion-exchange method in some instances is successful for producing the LIPs. However, in many instances the yields are low and incomplete exchange is noted. Treatment of the parent halide salts with a charge equivalent amount of 85% phosphoric acid, followed by complete evaporation of all volatile materials under reduced pressure over a period of a week provides LIPs in good yield and in a highly pure state. This approach provided the most efficient and reproducible route for the preparation of the LIPs and subsequently has been used for the preparation of a large series of significant quantities of a large series of these materials. All of the newly prepared liquid ionic phosphates exhibit ^1H , ^{13}C , and ^{31}P NMR spectra in total accord with their proposed structures.

The resultant materials are all water soluble, unlike the previously prepared non-aqueous ionic liquids bearing hexafluorophosphate anions or anions that are significantly water reactive. The thermal stability of the LIPs has been examined as a function of structure. Those materials that are saturated macrocycles with charged sites located within the macrocycle exhibit thermal stability at 160°C for 4 h or longer and bear potential as materials for use under stringent conditions. Similarly, linear structures with charged sites along the chain of the cations exhibit thermal stability as long as terminal functionalities are no more than three carbon atoms from a cationic site. Chains with longer tails terminating in functionality exhibit lower thermal stabilities. Electrochemical and spectroscopic characteristics of these new materials have been investigated and are reported elsewhere.