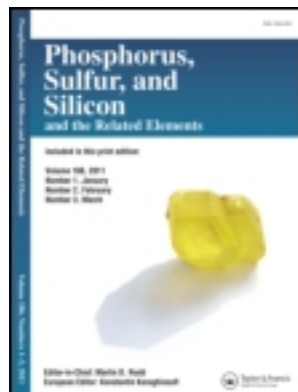


This article was downloaded by: [Kazan State University]

On: 15 May 2013, At: 02:24

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.tandfonline.com/loi/gpss20>

Synthesis of Phosphorylated Piperazines

N. G. Khusainova^a, E. P. Pogodina^a, E. A. Berdnikov^a, I. V. Galkina^a & V. I. Galkin^a

^a A. M. Butlerov Chemical Institute, Kazan Federal University, Kazan, Russia

Published online: 08 May 2013.

To cite this article: N. G. Khusainova, E. P. Pogodina, E. A. Berdnikov, I. V. Galkina & V. I. Galkin (2013): Synthesis of Phosphorylated Piperazines, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 188:1-3, 61-62

To link to this article: <http://dx.doi.org/10.1080/10426507.2012.741158>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

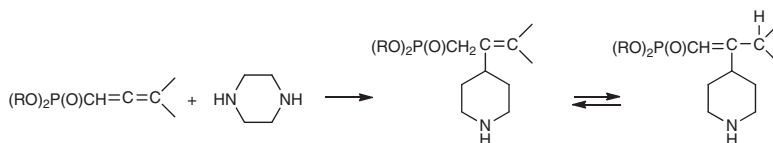
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for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

N. G. Khusainova, E. P. Pogodina, E. A. Berdnikov,
I. V. Galkina, and V. I. Galkin

A. M. Butlerov Chemical Institute, Kazan Federal University, Kazan, Russia

GRAPHICAL ABSTRACT



Abstract Heating 3-methyl-1,2-butadienyl phosphonates with piperazine leads to the formation of 2-piperazinyl-butenyl phosphonates containing the enamine functionality. From the reaction of piperazine with four equivalents of 1,2-butadienyl phosphonate a bis(phosphonate) is obtained, in which the piperazine bridge links two phosphorylbutene fragments.

Keywords Allenes; addition; 3-methyl-buta-1,2-dienyl phosphonates; piperazine; enamines

INTRODUCTION

The interest in the synthesis of polyfunctional organophosphorus compounds, in particular of β -aminoalkyl(alkenyl) phosphonates, originates from numerous possibilities for their practical application. Allenes, due to their unique reactivity, are important and versatile building blocks in the construction of various multifunctional compounds.

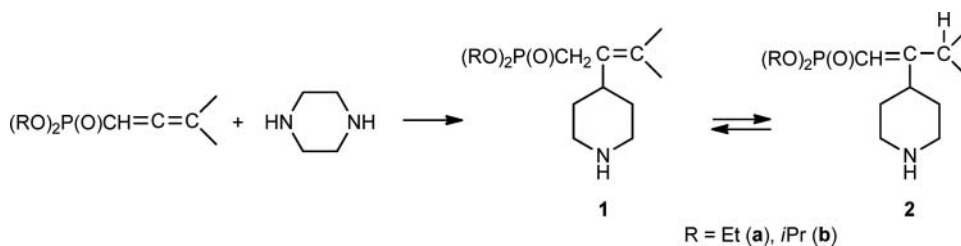
RESULTS AND DISCUSSION

Herein, we report the results of our study on the interaction of 3-methylbuta-1,2-dienyl phosphonates with piperazine. Heating of the reactants at 80°C for 1 h in the presence of a sodium alkoxide led to the formation of hygroscopic addition products, which according to their NMR spectra in $CDCl_3$ represent a mixture of tautomeric enamines (Scheme 1). The structure of the products was determined by 1H and ^{31}P NMR spectroscopy as well as by IR spectroscopic studies. Thus, in the 1H NMR spectra of the adduct of diethyl 3-methylbuta-1,2-dienylphosphonate and piperazine (yield 78%, bp 132°C–135°C (0.05 mm), $n_D^{20} = 1.4852$) a signal at $\delta = 2.63$ ppm (d, $^2J_{PH} = 21.9$ Hz, 2H, CH_2) is observed. It was assigned to the protons of the methylene group linked to the phosphorus atom; that is,

Received 16 July 2012; accepted 14 October 2012.

Address correspondence to N. G. Khusainova, A. M. Butlerov Chemical Institute, Kazan Federal University, Kazan, Russia. E-mail: narkis.khusainova@ksu.ru

addition of the amino nitrogen atom of piperazine occurred at the β -carbon atom of the butadienyl phosphonate. The signals of the $(\text{CH}_3)_2\text{C} =$ protons appeared as a two doublets at $\delta = 1.65$ ppm (d, $^5J_{\text{PH}} = 4.9$ Hz, 3H, CH_3) and at $\delta = 1.74$ ppm (d, $^5J_{\text{PH}} = 6.6$ Hz, 3H, CH_3); this corresponds to the addition of piperazine at 1,2-double bond of the butadienyl phosphonate. Thus, the enamine **1a** is present in the reaction mixture. The presence of a signal at $\delta = 3.93$ ppm (d, $^2J_{\text{PH}} = 8.7$ Hz, 1H, $\text{P}-\text{CH}=\text{C}$) and signals at $\delta = 1.18$ ppm (d, $^3J_{\text{HH}} = 7.3$ Hz, 6H, CH_3 , $(\text{CH}_3)_2\text{CH}-\text{C}$) and at $\delta = 3.70$ ppm (sept., $^3J_{\text{HH}} = 7.3$ Hz, 1H, $(\text{CH}_3)_2\text{CH}-\text{C}$) indicates also to the formation of the tautomeric enamine **2a** in the mixture. In the ^{31}P NMR spectrum of the adduct two signals at $\delta = 27$ ppm (major) and at $\delta = 24$ ppm (minor) are observed.



Scheme 1

The interaction of four equivalents of 3-methyl-buta-1,2-dienyl phosphonates with piperazine leads to the formation of bisphosphonates, which consist of two phosphoryl-butene groups symmetrically linked to each other by the piperazine bridge. Their ^1H NMR spectra differed from the spectra of the 1:1 adducts by the signal intensity ratio and the absence of the broad singlet at $\delta = 2.26$ ppm (NH).

It was found that the reaction of 3-methyl-buta-1,2-dienyl phosphonates with 2-aminoethyl piperazine involves the addition of the primary exocyclic amino group to the sp-hybridized carbon atom of the phosphorylallene and leads also to a mixture of tautomeric enamines. The adducts show fungicide activity.