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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

General Approach for Regioselective Synthesis of Fused Phosphono Substituted-Heterocycles. Reactions of Bismethylene-1,3-dithietane with H -Nucleophiles

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Online publication date: 27 October 2010

To cite this Article Abdou, Wafaa , Elkhoshnieh, Yehia and Ganoub, Neven(2002) 'General Approach for Regioselective Synthesis of Fused Phosphono Substituted-Heterocycles. Reactions of Bismethylene-1,3-dithietane with H -Nucleophiles', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 6, 1885 — 1888

To link to this Article: DOI: 10.1080/10426500212250 URL: http://dx.doi.org/10.1080/10426500212250

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Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1885–1888 Copyright © 2002 Taylor & Francis 1042-6507/02 \$12.00 + .00

DOI: 10.1080/10426500290093153



GENERAL APPROACH FOR REGIOSELECTIVE SYNTHESIS OF FUSED PHOSPHONO SUBSTITUTED-HETEROCYCLES. REACTIONS OF BISMETHYLENE-1,3-DITHIETANE WITH H-NUCLEOPHILES

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

A number of [2,1-b] fused phosphono substituted-thioxopyranes, -oxadiazines, and -thiazines were obtained from the reactions of the corresponding α -carbonyl methylenes and α -carbonylmonohydrazones with phosphenato-substituted 1,3dithietane 1.

Keywords: Heterocyclization; phosphono substituted-heterocycles; polyfunctional organophosphorus compounds

INTRODUCTION

Lately the development of organophosphorus chemistry has been characterized by a great interest in the substituted-cyclic derivatives. On the whole they may be obtained by the phosphory-lation of polyfunctional organic and organoelement substrates or by intramolecular transformations of polyfunctional organophosphorus derivatives. In the course of our research for new phosphono substituted-heterocycles with good biological and/or pharmacological activities, a series of phosphono substituted-thioxopyran, -oxadiazine, and -thiazine systems are now synthesized as described in this article. Our approach involves the condensation of 1,3-dithietane-2,4-diylidene-bis(cyanomethylphosphonate) 1 with different types of $\underline{\mathbf{H}}$ -nucleophiles such as cyclic and acyclic α -carbonylmethylenes and α -carbonylmonohydrazones.

RESULTS AND DISCUSSION

The procedure of the reaction of 1,3-dithietane 1 with \underline{H} -nucleophiles is closely analogous to that previously reported by Neidlein et al.² for

the reaction of 1 with acetonitriles. Typically, the phosphorus reagent 1 dissolved in absolute ethanol was treated with $NaOC_2H_5$ followed by the addition of the substrate (2 molequiv.). The reaction mixture was then poured onto iced water and acidified. The products were easily separated by solvent extraction and purified by chromatography.

According to this procedure, treatment of **1** with 1,3-indanedione **2** (2 moleguiv) at r. t. for 3 h led to the formation of **3** (74%) (Scheme 1).

H
H
H

(EtO)₂P
S
CN
P(OEt)₂

1

NC
O
NC
O
NC
O
NC
C-P(OEt)₂

A

3,
$$\delta p = 14.6 \text{ ppm}$$

SCHEME 1

Similar to **3**, the phosphonate **5** (68%) was readily obtained by allowing **1** to react with 4-hydroxycoumarin **4** (Scheme 2).

SCHEME 2

Conversely, the reaction of **1** with thiazolidinone **6** proceeded under more drastic conditions, by heating the reaction mixture under reflux for 5 h to give the phosphono substituted-thioxopyran **7** (48%) (Scheme 3).

$$\begin{array}{c|c}
HN & +1 \\
S & H
\end{array}$$

$$\begin{array}{c|c}
HN & O & NH_2 \\
S & S & P(OEt)_2
\end{array}$$

$$\begin{array}{c|c}
HN & O & NH_2 \\
O & P(OEt)_2
\end{array}$$

$$\begin{array}{c|c}
A & 7, \delta p = 14.6 \text{ ppm}
\end{array}$$

SCHEME 3

2-Thiohydantoin **8**, which is less reactive than the above three mentioned $\underline{\mathbf{H}}$ -nucleophiles, reacted with **1** in ethanol under reflux temp. for 12 h yielding the phosphonate **9** in 62% yield (Scheme 4).

O H H
$$+1$$
 NaOEt/ \triangle S NH O P(OEt)₂ S O SH CN

8 9, $\delta p = 19.5 \text{ ppm}$

SCHEME 4

Finally, the phosphorus reagent **1** was applied to an acyclic substrate **10** in boiling ethanol for 5 h, whereby the thioxopyranphosphonate **11** (57%) was obtained (Scheme 5).

$$\begin{array}{c|c} & & & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

SCHEME 5

Next, the reactions of **1** with α -carbonylhydrazones were investigated. When an ethyl alcohol solution of acenaphthenequinonemonohydrazone **12** and a half equivalent of 1,3-dithietane **1** was heated under reflux for 6 h, the fused oxadiazine **13** (56%) and the known³ ketazine (12%) were obtained according to Scheme 6.

SCHEME 6

A parallel oxadiazinylidenecyanomethylphosphonate **14** (64%) was obtained as the sole reaction product from the reaction of 3,5-di-*tert*-butylbenzoquinone with diethietane **1**. On the other hand, pyrazolyl phosphonate **15** (49%), along with the expected 1,3,4-oxadiazine derivative **16** (11%), were obtained from the reaction of 1,3-Indandione-2-hydrazone with the same reagent.

It should be noted that all assigned structures are confirmed by a thorough study of their elemental analyses, mass measurements, and spectroscopic data (IR, ¹H, ¹³C, and ³¹P-NMR).

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