This article was downloaded by:

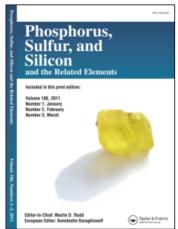
On: 30 January 2011

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

## Salts of $\alpha$ -Diazo "Phosphorus Acids" - Starting Compounds for Phosphonate and Phosphate Transfer Reagents

Manfred Regitz<sup>a</sup>; Roland Martin<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Kaiserslautern, Kaiserslautern, Germany

To cite this Article Regitz, Manfred and Martin, Roland(1983) 'Salts of  $\alpha$ -Diazo "Phosphorus Acids" - Starting Compounds for Phosphonate and Phosphate Transfer Reagents', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 163 — 166

To link to this Article: DOI: 10.1080/03086648308075992 URL: http://dx.doi.org/10.1080/03086648308075992

## 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.

SALTS OF  $\alpha\text{-DIAZO}$  "PHOSPHORUS ACIDS" - STARTING COMPOUNDS FOR PHOSPHONATE AND PHOSPHATE TRANSFER REAGENTS

MANFRED REGITZ AND ROLAND MARTIN
Department of Chemistry, University of Kaiserslautern,
Erwin-Schrödinger-Straße, D-6750 Kaiserslautern, Germany

Abstract Pyrazoles bearing N-phosphonate and phosphate groups are well accessible from salts of  $\alpha$ -diazo "phosphorus acids" and electron poor acetylenes. They are good phosphorylating reagents for protic nucleophiles.

The  $\alpha$ -diazophosphinates  $\underline{1}$  - well accessible by diazo group transfer or by electrophilic diazoalkane substitution - are transformed into the trimethylsilylesters  $\underline{2}$  without destruction of the diazo group by treatment with bromo trimethylsilane  $^1$ . They are extremely sensitive against water and decompose under desilylation and  $N_2$ -loss to form the  $\alpha$ -hydroxyphosphinic acids  $\underline{3}$ .

In contrast to that and without attack of the diazo unit the silylesters  $\underline{2}$  can be solvolysed with two equivalents of tertbutyl amine to yield the hitherto unknown ammonium  $\alpha$ -diazophosphinates 4.

In an analogous way the  $\alpha$ -diazophosphonates  $\underline{5}$  react with bromo trimethylsilane followed by tert-butyl amine treatment either to the ammonium methyl  $\alpha$ -diazophosphonates  $\underline{6}$  or to the bis(ammonium)  $\alpha$ -diazophosphonates  $\underline{7}$  depending on the molar ratio of both reaction partners. The cleavage of the second methoxy group only takes place at elevated temperature.

The constitution of the new diazo compounds is based on the analytical data and on ir,  $^1\text{H-}$ ,  $^{13}\text{C-}$  and  $^{31}\text{P}$  n.m.r. evidence.

Chemical arguments for the constitution of the diazo salts examplarily are given for  $\underline{10}$ . Methylation with diazomethane to  $\underline{8}$  and acylation with acetyl chloride leading to the mixed anhydride  $\underline{9}$  leave the diazo group unattacked.

In contrast to that the photolysis of  $\underline{10}$  in methanol such as the reaction with the strong electrophile 1-pheny1-1,3,4-triazo-line-2,5-dione in the presence of ethanol proceeds under the loss of the diazo nitrogen (formation of  $\underline{11}$  and  $\underline{12}$ ).

The transformation of the diazo salts  $\frac{4}{2}$  into phosphonate group transferring reagents is accomplished by [3+2] cycloaddition reaction with methyl propiolate, in the first step leading to the non isolable 3H-pyrazole  $\frac{13}{2}$ .

Subsequent [1,5]-sigmatropic phosphoryl group migration <sup>2</sup> produces the actual phosphorylating reagent 15.

Protic nucleophiles HX like amines or alcohols are phosphory-lated by  $\underline{15}$  under smooth conditions (formation of the phosphonates  $\underline{16}$ ).

An analogous reaction sequence is unsuccessful for the production of the corresponding phosphate group transferring reagent: The cycloaddition reaction between the same acetylene and  $\underline{6}$  leading to  $\underline{14}$  is followed by a series of signatropic PO- and H-migrations, which in the last consequence afford the NH-pyrazole  $\underline{17}$ .

Nevertheless the [3+2]-cycloaddition reaction with 6 and dimethyl acetylene dicarboxylate instead of methyl propiolate produces the true phosphorylating pyrazole (15: OMe instead of Ph and CO<sub>2</sub>Me instead of CH-Pyrazole). Alcohols, amines and hydrazines are phosphorylated without complications to the corresponding phosphates; 2-aminoethanol is selectively phosphorylated at the more nucleophilic amino group.

## REFERENCES

- c.f. J.A.Goldstein, C.McKenna and F.H.Westheimer, <u>J.Am.Chem. Soc.</u> 98, 7327 (1976); P.A.Bartlett and K.P.Long, <u>J.Am.Chem. Soc.</u> 99, 1267 (1977).
- A. Hartmann and M. Regitz, <u>Phosphorus</u> 1974, 21; U.-H. Felcht and M. Regitz, <u>Angew. Chem. 88</u>, 377 (1976); <u>Angew. Chem., Int. Ed. Engl.</u> 15, 378 (1976).